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THERMOELECTRICITY

QUARTERLY PROGRESS REPORT NO. 2

U. S. NAVY

BUREAU OF SHIPS
WASHINGTON 25, D.C.

MAY - AUGUST, 1962

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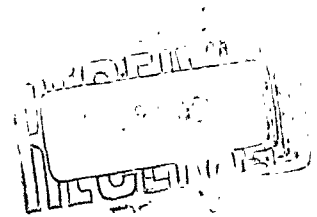
Westinghouse Electric Corporation

CENTRAL RESEARCH LABORATORIES   PITTSBURGH 35, PA.

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CONTENTS

I. SUMMARY

Effort on new material development during the period has been confined to the Co-Sb system. Further evidence has been obtained for the possibility of developing matched "p" and "n" materials that will have mechanical properties conducive to reliability with moderate conversion efficiency.

The first report, $Sb_{2-x}Bi_xTe_3$ Alloys for Thermoelectric Power Generation, summarizes the development work on this series of alloys. Compositions, processing, and contacting methods are presented. Alloys have been optimized for use at hot side temperatures up to 425°C. No further alloy development is planned; however, testing will be continued to provide data for application of these alloys.

The report entitled, The Preparation and Evaluation of Indium-Antimony-Tellurium Alloys for Thermoelectric Power Generation, likewise summarizes the work on this alloy system. Testing will continue, but no further development will be done.

The last two reports, Vaporization of Zinc Antimonide and The Vapor Pressure of Germanium Telluride, provide additional data pertinent to the application of these materials.

II. MATERIAL DEVELOPMENT

$CoSb_{3-x}M_x$ Alloys

Essentially, the development work on "n"-type cobalt antimonide alloys has been completed. The figure of merit of the tellurium doped cobalt antimonides has been improved through the addition of selenium to lower the thermal conductivity, as can be seen from the table:

	$\alpha(\mu V/°C)$ 550-150°C	$\rho \times 10^3 (\Omega\text{-cm})$ 550-150°C	K(Watts/cm-°C) Room Temp.
$CoSb_3$	-212*	10.38*	0.079
$CoSb_{2.85}Te_{.15}$	-182	0.84	0.048
$CoSb_{2.6}Te_{.1}Se_{.3}$	-181	1.38	0.027

In addition to good electrical properties, cobalt antimonide alloys appear to possess very good mechanical properties. Specifically, the "n"-type alloys are strong stable materials which will not readily oxidize in air at 550°C. A combination of low coefficient of thermal expansion (10.0×10^{-6} in/in/°C) and a relatively high thermal conductivity make these alloys insensitive to thermal shock.

Undoped $CoSb_3$ has been shown to be "p" type by Battelle Memorial Institute if contamination by oxygen can be avoided. The "n"-type $CoSb_3$ in the above table is believed to show the effect of oxygen and perhaps nickel contamination. The Battelle researchers have been able to make a "p"-type $CoSb_3$ with $\bar{\alpha} = +214 \mu V/°C$ and $\bar{\rho} = 4.20 \times 10^{-3} \Omega\text{-cm}$ over a 450°C temperature range.

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* ΔT: 450-150°C

To circumvent the oxygen problem, $CoSb_3$ alloys are being prepared by induction melting under hydrogen. However, preliminary results indicate that hydrogen is also an "n"-type dope, and experiments are now underway to determine the feasibility of degassing the liquid alloy under vacuum. Recently, $CoSb_3$ with a low but positive Seebeck coefficient has been made. It is hoped that the use of special low nickel cobalt (nickel being a "n"-type dope) and vacuum melting techniques will improve the properties so that they can be adjusted by doping.

Materials Development

EQUIPMENT & SYSTEMS TECHNOLOGY

REPORT NO. 62-964-242-R1

$Sb_{2-x}Bi_xTe_3$ ALLOYS FOR THERMOELECTRIC POWER GENERATION

Abstract

A series of p-type alloys of the form $Sb_{2-x}Bi_xTe_3$ have been developed for thermoelectric power generation in the temperature range 0° to 450°C. Pellets of these alloys are readily prepared by powder metallurgical techniques and are easily joined to form couples. As the p-leg in couples still on test, they have withstood over 1000 hours of operation while undergoing more than 250 thermal cycles. A four-couple test module has been on test 2000 hours and is still functioning with only slight degradation.

J. P. McHugh

July 18, 1962

Introduction

One of the major problems in the practical utilization of thermo-electricity for power generation has been the lack of a p-type material capable of operating for long periods of time under generator conditions without significant degradation in thermoelectric properties. By generator conditions, we mean that the material is joined at the hot and cold sides, operates under a steep temperature gradient, and undergoes numerous on-off thermal cycles. The objective of the work described in this report was to develop and test a p-type thermoelectric material having a practically useable efficiency and which is capable of operating in an inert atmosphere in a generator for 10,000 hours and undergoing 100 thermal cycles with less than 25% degradation in power output. A series of alloys of the form $Sb_{2-x}Bi_xTe_3$, $0 < x < 0.5$, which appears to satisfy these requirements has been developed. Several of these alloys have average values of

$$Z = \frac{S^2}{\rho K} > 1 \times 10^{-3}$$

when operated over a ΔT of $100°$ to $425°C.$, and even higher when operated with lower cold side temperatures. Simple powder metallurgical techniques, easily extendable to mass production, were used to prepare quantities of these alloys for testing. A joining technique for preparing couples was also developed.

Before describing the procedures developed and the test results obtained in this investigation, we wish to discuss briefly some background information and a few ideas of importance here and in thermoelectric alloy development in general.

Bismuth telluride, Bi_2Te_3, and antimony telluride, Sb_2Te_3, form a continuous series of solid solutions,[1] all compositions having the rhombohedral tetradymite structure and exhibiting easy cleavage along the

(111) planes. The maximum in the liquidus in both the Bi-Te system and the Sb-Te systems occurs off the stoichiometric composition on the Bi rich side, corresponding to $Bi_{40.065}Te_{59.935}$ and $Sb_{40.4}Te_{59.6}$[2]. There is a continuous change in carrier concentration (and therefore thermo-electric properties) as alloy composition progresses from one end member to the other in the Sb_2Te_3-Bi_2Te_3 pseudo binary system. It is there-fore possible to vary the thermoelectric properties over a considerable range by varying the Sb_2Te_3-Bi_2Te_3 ratio without the use of additional elements or compounds as doping agents.

Because of their crystal structure, these alloys exhibit aniso-tropy of electrical properties. The electrical resistivity is considerably lower in the cleavage direction than in any other direction. The best thermoelectric properties are obtained by using the alloy in such a way that current flow is in a direction parallel to the cleavage planes. Ideally, single crystals would be desirable in order to obtain 100% desired orientation. But, because of cost, processing difficulties and mechanical characteristics, single crystals are not practical. However, it is possible to retain a large degree of anisotropy in pellets prepared by the more practical powder metallurgical techniques if a few simple precautions are observed in the processing.

Processing bears an important role in determining the thermoelectric properties of an alloy.[3,4] Various processing techniques may have the effect of introducing or removing charge carriers, either positive or negative, or introducing or removing scattering centers[4], relative to some other process-ing techniques. For this reason, comparisons of the effects of varying alloy

composition are valid only if the processing has been invarient. Electrical properties observed on a sample prepared by powder metallurgical techniques may differ by orders of magnitude from those observed on a single crystal of the same nominal chemical composition. The development of a useful thermo-electric alloy therefore requires the consideration of chemical composition and processing together as complementary and inseparable.

Experimental

The experimental work involved in this investigation may be conven-iently divided into three categories: material processing, joining, and testing.

a). Material Processing

A powder metallurgical technique was selected for processing because of its easy extension to mass production, its economy, and its nearly 100% yield of pellets of uniform thermoelectric properties. The following procedure was used. Heats of 500 grams total weight were prepared by melting together the proper amounts of 99.99$^+$% pure elements in a Balzer furnace under argon, using graphite crucibles. Induction heating provided stirring of the melt and permitted rapid heating, thus minimizing volatility losses. Within 5 to 7 minutes the crucible charge reached a temperature of 700 to 750°C, at which point the molten alloy was quenched by pouring onto a graphite coated copper slab. The entire operation was carried out under pure argon.

As mentioned previously, these Sb-Bi-Te alloys are highly anisotropic, and it is desirable to maintain as much of this anisotropy as possible in the final pressed pellet. In grinding, the cast alloy will tend to cleave along

the natural cleavage planes to form platelets. These platelets will tend to align in the dies during filling and pressing. It is therefore important not to overgrind and destroy this platelet structure. For this reason, ball milling is not a satisfactory method of grinding. It is better to use a jaw crusher or small-batch hand grinding.

In the present investigation, hand grinding was used to reduce the cast alloys to powder. Material of -60 mesh was used to prepare pellets by cold pressing at 35 tsi. Rectangular dies were used since the pellets must be oriented in devices so that the current path is perpendicular to the pressing direction to achieve the best thermoelectric properties. Our procedure yields sufficient preferred orientation to produce a marked difference in electrical resistivity between directions parallel to and perpendicular to the pressing direction. The cold pressed pellets were then annealed in pure argon for three hours at 450°C. Higher compacting pressures and/or higher annealing temperatures are not advisable because of the danger of the pellets swelling during the annealing operation.

b). Joining

In order to obtain operating data on new materials (and to subsequently use them in devices), it is necessary to fabricate couples. This involves joining the pellets to straps on the hot side and to caps on the cold side. These joints must have low electrical and thermal resistance and maintain these characteristics after operation at the required temperatures for long periods of time and through numerous thermal cycles. The following procedure was found to satisfy these requirements.

A typical test couple is shown schematically in Fig. 1. The hot side of the p-legs were plasma sprayed with 3 mils Cr followed by a 1 mil flash of Ni. The n-legs, consisting of ordinary pressed and sintered PbTe + 0.1% Bi, were plasma sprayed on the hot side with 3 mils Co followed by a 1 mil flash of Ni. The hot side joining alloy for both legs was the 41 wt.% In-59 wt.% Au eutectic alloy (494°C m.p.). Cold pressed pre-forms, 10 to 15 mils thick, were prepared from 325 mesh powder of the joining alloy. The silver hot straps, pre-forms, and pellets were mounted in a jig with spring loading, heated in a hydrogen atmosphere to 500°C, held at that temperature for ten minutes, and cooled in hydrogen. The copper cold caps and braids were then joined to the cold sides of both legs ultrasonically using pure tin as solder.

c). Testing

Three phases of testing were involved in this investigation: (1) testing of electrical and thermal properties of individual pellets in order to determine the best alloys, (2) testing of single couples to assess operating characteristics and operating life of the new p-materials, and (3) testing of modules of four couples each to assess operating characteristics and operating life under conditions approaching those found in a thermoelectric generator.

Individual pellet testing included measurement of average Seebeck coefficient, S, and resistivity, ρ, over a large ΔT, measurement of S and ρ as a function of temperature, measurement of thermal conductivity (generally at room temperature) and a determination of thermal expansion coefficient. Several single couples were tested in an argon atmosphere to test material

characteristics under operating conditions and to assess the ability of both the thermoelectric materials and the joints to withstand repeated thermal cycling. During couple tests, Seebeck coefficient, resistance, and power output were monitored for both the p and n legs by means of thermocouple leads placed in the hot strap and in the cold caps of each leg. Readings were taken daily. A pair of modules, each containing four couples, were constructed and tested in argon to determine the effects of the additional mechanical and thermal variables involved when several couples are mounted in series. Total power output from the modules was measured weekly.

Results

Results are summarized in Tables I to III and Figs. 2 to 7. All measurements on the pressed and sintered pellets were made with Δ T's and current flow perpendicular to the pressing direction. Table I lists values for room temperature thermal conductivity and average values of S and ρ measured over Δ T's of 100°-400°C and 150°-450°C for a number of alloys. Figs. 2 and 3 show S and ρ measured as a function of temperature from room temperature to 500°C for four alloy compositions. Fig. 4 shows ρ , S, K and Z (calculated) for the $Sb_{1.7}Bi_{0.3}Te_3$ alloy from room temperature to 150°C, measured by an absolute method. Note that this alloy has a Z of 2.3×10^{-3} at room temperature and that Z is still about 2×10^{-3} at 150°C.

Table II briefly summarizes some life test data obtained thus far on a number of samples of heat 3341 ($Sb_{1.7}Bi_{0.3}Te_3$) tested as the p-leg in couples prepared as shown in Fig. 1. Figs. 5 and 6 show measured resistance and power

for both the p and n-legs separately, as well as total power output for the same couples as a function of operating time. During most of the operating time, these couples were thermal cycled at three hour intervals.

Table III lists pertinent data for a pair of four-couple modules containing couples constructed as shown in Fig. 1. Note that the area to length ratio of the couples in module no. 2 is a factor of four greater than that of the couples in module no. 1. The cold side temperature of the couples in these modules is not monitored and is estimated to be about 150°C on module no. 1 and about 115°C on module no. 2. The average hot side temperatures are approximately 425°C. The total resistance and total power output only are being monitored on these modules, and the values of these parameters as a function of time are shown in Fig. 7.

Unless otherwise indicated, these couples and modules are still under test. Note that all life testing has been done in an argon atmosphere. These p-materials cannot be operated in air without a suitable encapsulant (which has not yet been developed).

The thermal expansion coefficient for pressed and sintered pellets of alloy 3341 ($Sb_{1.7}Bi_{0.3}Te_3$) in the direction perpendicular to the pressing direction, averaged for the temperature interval of 100° to 400°C, was determined as 17.5 x 10^{-6}/°C and 18.0 x 10^{-6}/°C for heating and cooling respectively.

Discussion

We can see from the thermoelectric property measurements that over a small composition range, $Sb_{2-x}Bi_xTe_3$ alloys provide p-type thermoelectric

power generation materials for use in the temperature range of room temperature to about 450°C with a Z of 1.0 x 10⁻³ or more averaged over the temperature range. Variations in composition cause variations in resistivity which permit, within limits, the production of couples with matched n and p-legs. While these alloys are comparable in efficiency when operated over a ΔT of about 100°-425°C to most other power generation alloys, both n and p, now available, they would have a distinct material efficiency advantage over other materials when used in applications requiring lower cold side temperatures, lower hot side temperatures, or both.

However, efficiency is only of academic interest unless a material is capable of operating for long periods of time without rapid degradation under generator conditions. From the point of view of life time, the $Sb_{2-x}Bi_xTe_3$ alloys appear most promising. Two single couple tests, using $Sb_{1.7}Bi_{0.3}Te_3$ (heat 3341), show essentially zero degradation in power output and resistance for the p-legs after more than 1000 hours of operation and 250 thermal cycles (Figs. 5 and 6 and Table II). Essentially all of the couple degradation thus far has been caused by an increase in the resistance of the PbTe n-legs.

In order to achieve maximum power output, the n and p-legs should have matched resistances. The particular batch of PbTe used for n-legs in these test couples does not match the resistance of the p-materials being tested too well, and it was used simply because it was available. However, even with this resistance mis-match, the PbTe n-leg still permits a realistic

evaluation of the operating life times of the p-materials which are the actual subject of this investigation.

The results obtained thus far on the pair of four-couple modules are quite encouraging. The degradation in power for module No. 1 amounts to about 5% after 2000 hours and 13 cycles, while that for module No. 2 is about 4% after 1000 hours and 5 cycles. The apparent degradation in module No. 2 is due at least in part to an estimated 10° to 20° decrease in the Δ T with time. Considering the results on the single couple tests, where the p-legs are monitored separately, the degradation in total power of the four-couple modules is probably due principally to degradation of the PbTe n-legs.

The test data obtained thus far lead us to believe that the object of this investigation, i.e., the development of a p-type thermoelectric power generation material capable of operating 10,000 hours with 100 thermal cycles in an inert atmosphere, has been met.

Conclusions

1. A series of promising p-type thermoelectric power generation alloys of the form $Sb_{2-x}Bi_xTe_3$ for use in the temperature range 0° to 450°C have been developed.

2. A powder metallurgical process for the preparation of these alloys in the form of rectangular pellets has been developed.

3. Variations in composition permit the matching of leg resistances in couples, within limits, and the optimization of efficiency over the desired operating ΔT.

4. These alloys withstand severe thermal shock without cracking.

5. A technique for joining pellets of these alloys to straps to form couples using a gold-indium joining alloy has been developed.

6. These alloys are capable of withstanding at least 250 thermal cycles without degradation.

7. These alloys are capable of operating at least 1000 hours in argon without degradation.

References

1. J. P. McHugh, unpublished results.

2. G. Offergeld and J. Van Cakenberghe, J. Phys. Chem.
    Solids 11, 310-4 (1959).

3. G. J. Cosgrove, J. P. McHugh and W. A. Tiller, J. Appl.
    Phys. 32 621-3 (1961).

4. J. M. Schultz, J. P. McHugh and W. A. Tiller, in publi-
    cation, J. Appl. Phys. (1962).

TABLE I - Thermoelectric Properties of Some $Sb_{2-x}Bi_xTe_3$ Alloys

Heat No.	Composition	K 30°C Watts/°/Cm	$\rho_{100-400}$,ohm cm	Large Δ T Averages		
				$S_{100-400}$, μV	$\rho_{150-450}$,ohm cm	$S_{150-450}$ μV
3265	Sb_2Te_3	0.033	0.78×10^{-3}	125	1.09×10^{-3}	137
3340	$Sb_{1.8}Bi_{0.2}Te_3$	0.026	0.86×10^{-3}	138	1.02×10^{-3}	145
3341	$Sb_{1.7}Bi_{0.3}Te_3$	0.016	1.51×10^{-3}	172	1.70×10^{-3}	163
3342	$Sb_{1.6}Bi_{0.4}Te_3$	0.015	1.89×10^{-3}	180	2.01×10^{-3}	165
3266	$Sb_{1.5}Bi_{0.5}Te_3$	0.013	2.04×10^{-3}	145	2.65×10^{-3}	132

TABLE II. Life Test for p-legs Tested in Couples

Couple No.	J - 4	J - 8	J - 9
Composition	$Sb_{1.7}Bi_{0.3}Te_3$	$Sb_{1.7}Bi_{0.3}Te_3$	$Sb_{1.7}Bi_{0.3}Te_3$
Size, L x W x H, inches	1/4 x 1/2 x 3/8	1/4 x 1/4 x 1/2	1/4 x 1/2 x 1/4
A/L	0.85	0.32	1.27
Braid Diameter	32,000 circ. mils	4000 circ. mils	32,000 circ. units
T_h, °C	425	425	425
T_c, °C	100	100	100
Initial Power, Watts (at 24 hours)	0.33	0.13	0.44
Recent Power, Watts	0.35 @ 700hr., 102 cy.*	0.14 @ 1065 hrs., 252 cy.	0.44 at 1155 hrs., 250 cy.

* Test discontinued because of entrance of air into test system.

TABLE III. Test Module Data

Module #	#1 (x-12)	#2 (x-15)
No. Couples	4	4
Composition, p-leg	$Sb_{1.7}Bi_{0.3}Te_3$	$Sb_{1.6}Bi_{0.4}Te_3$
Composition, n-leg	PbTe + 0.1 % Bi	PbTe + 0.1% Bi
Leg Size, L x W x H	1/4 x 1/4 x 1/2	1/4 x 1/2 x 1/4
A/L	0.32	1.27
Braid Diameter	4000 circ. mils	32,000 circ. mils

Silver Hot Strap
Au-In Joining Alloy
1 mil Plasma Sprayed Ni
3 mils Plasma Sprayed Co
n-leg (PbTe)
Sn Solder Joint
Cu Cold Cap

Cu Braid

Hot Side
Thermocouple Hole

Au-In Joining Alloy
1 mil Plasma Sprayed Ni
3 mils Plasma Sprayed Cr
p-leg ($Sb_{2-x}Bi_xTe_3$)
Sn Solder Joint

Cu Cold Cap
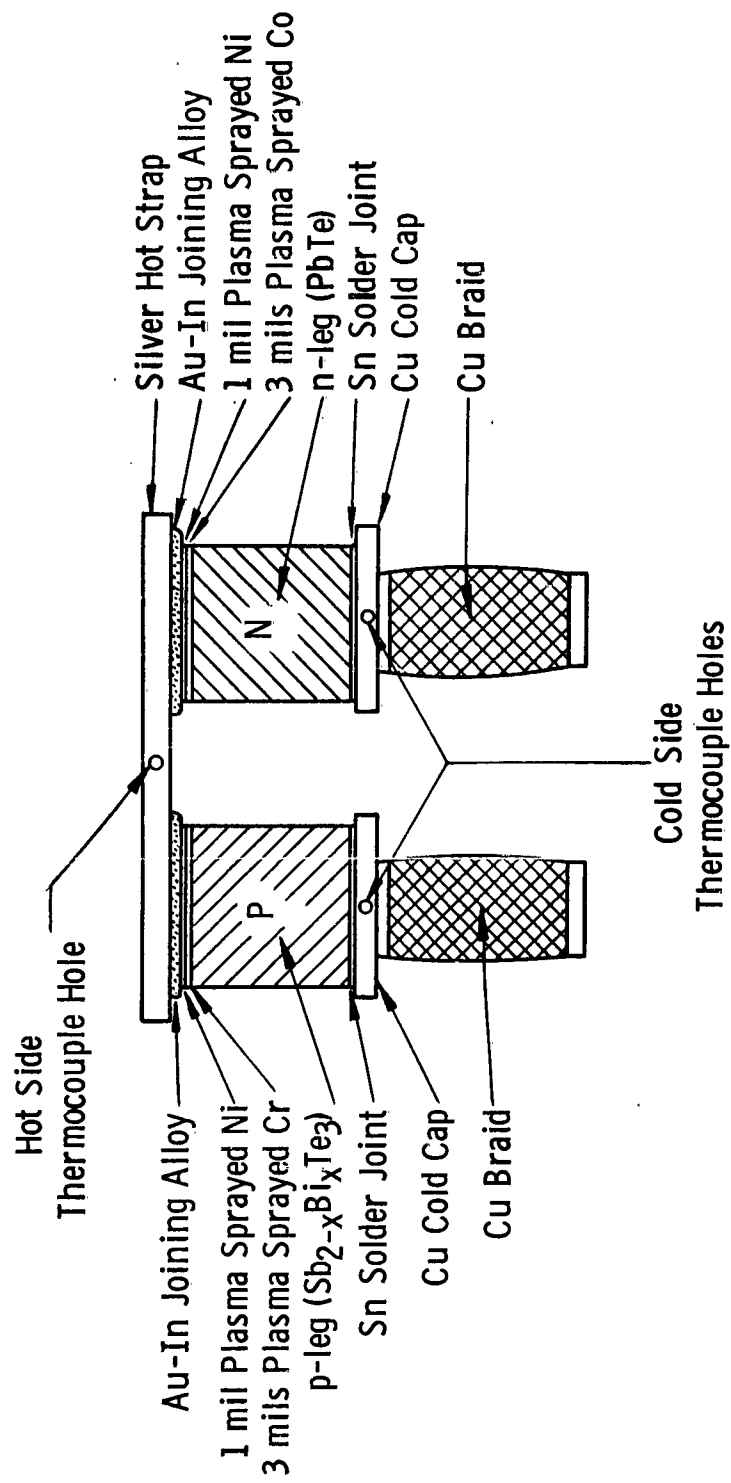
Cu Braid

Cold Side
Thermocouple Holes

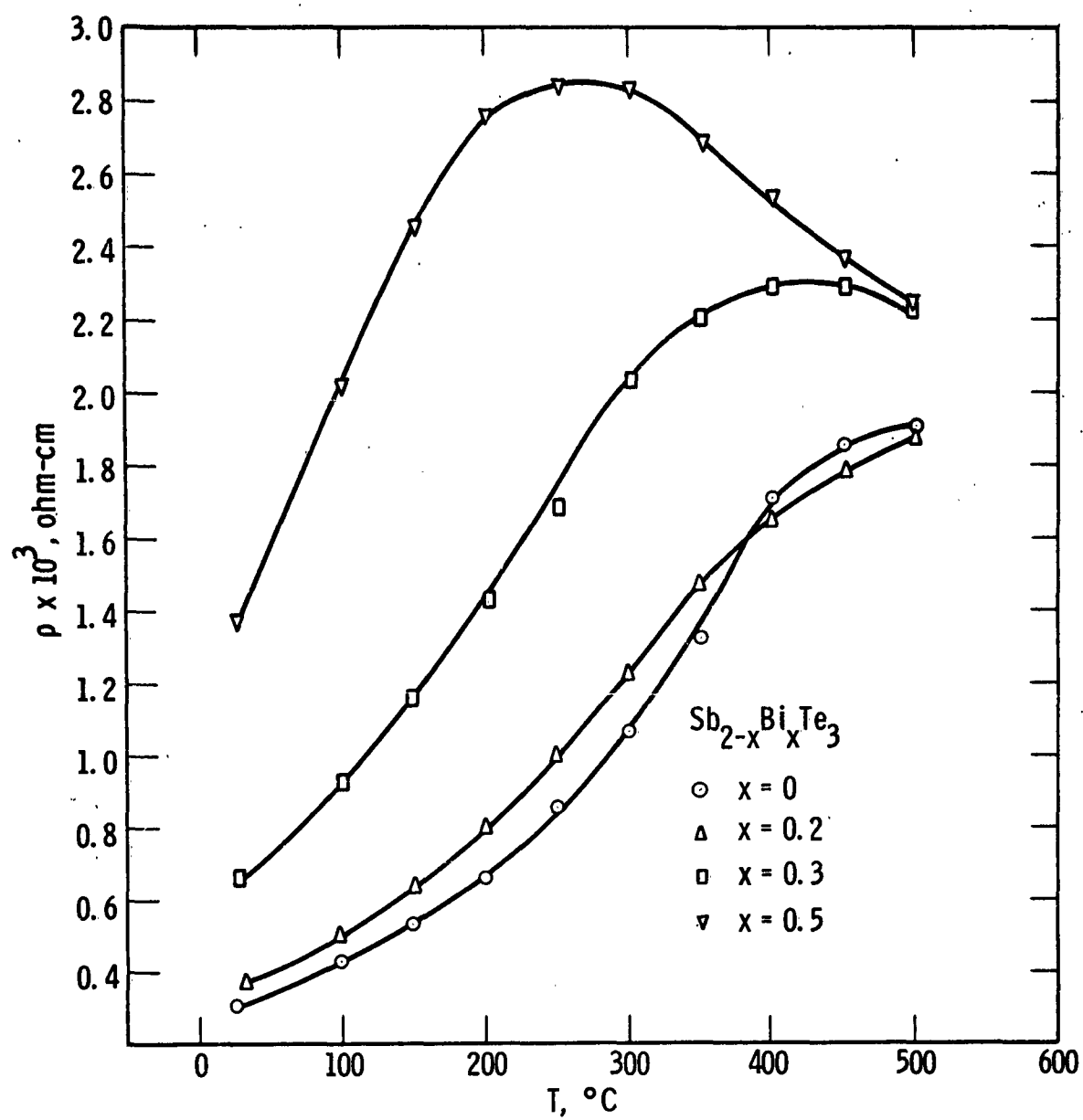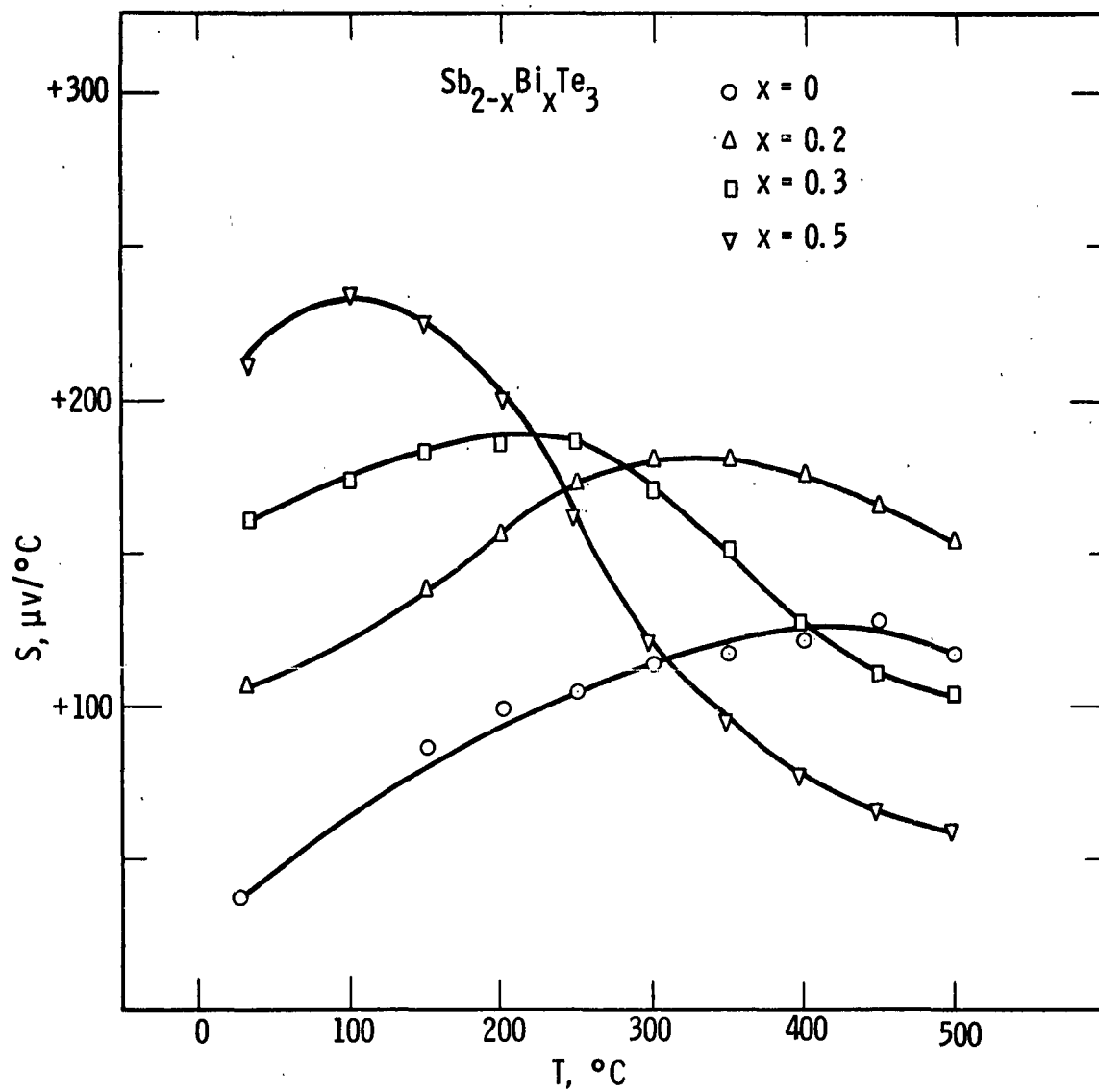Fig. 1—Schematic drawing of test couple, showing details of construction

Fig. 2—Resistivity vs. temperature

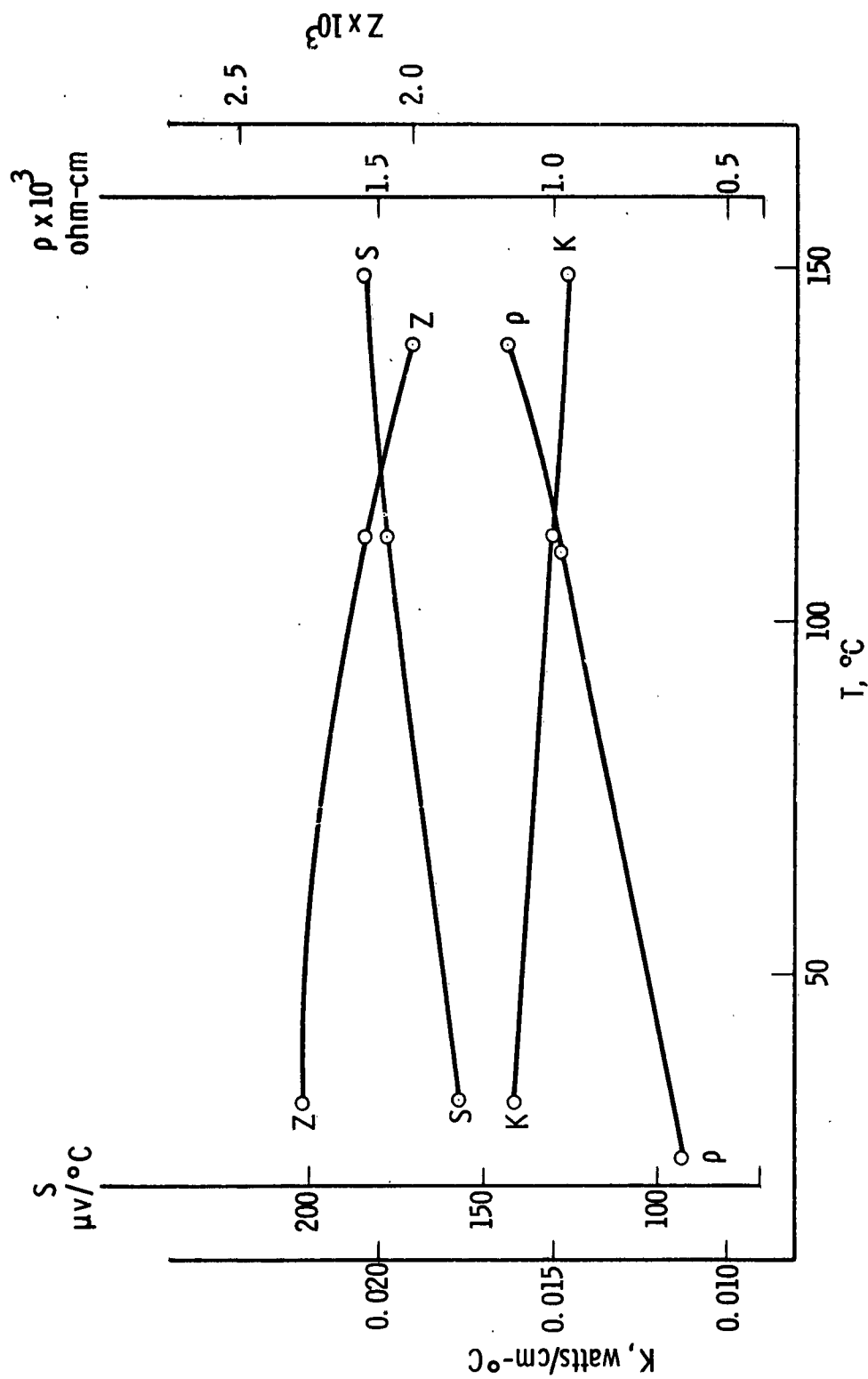Fig. 3—Seebeck coefficient vs. temperature

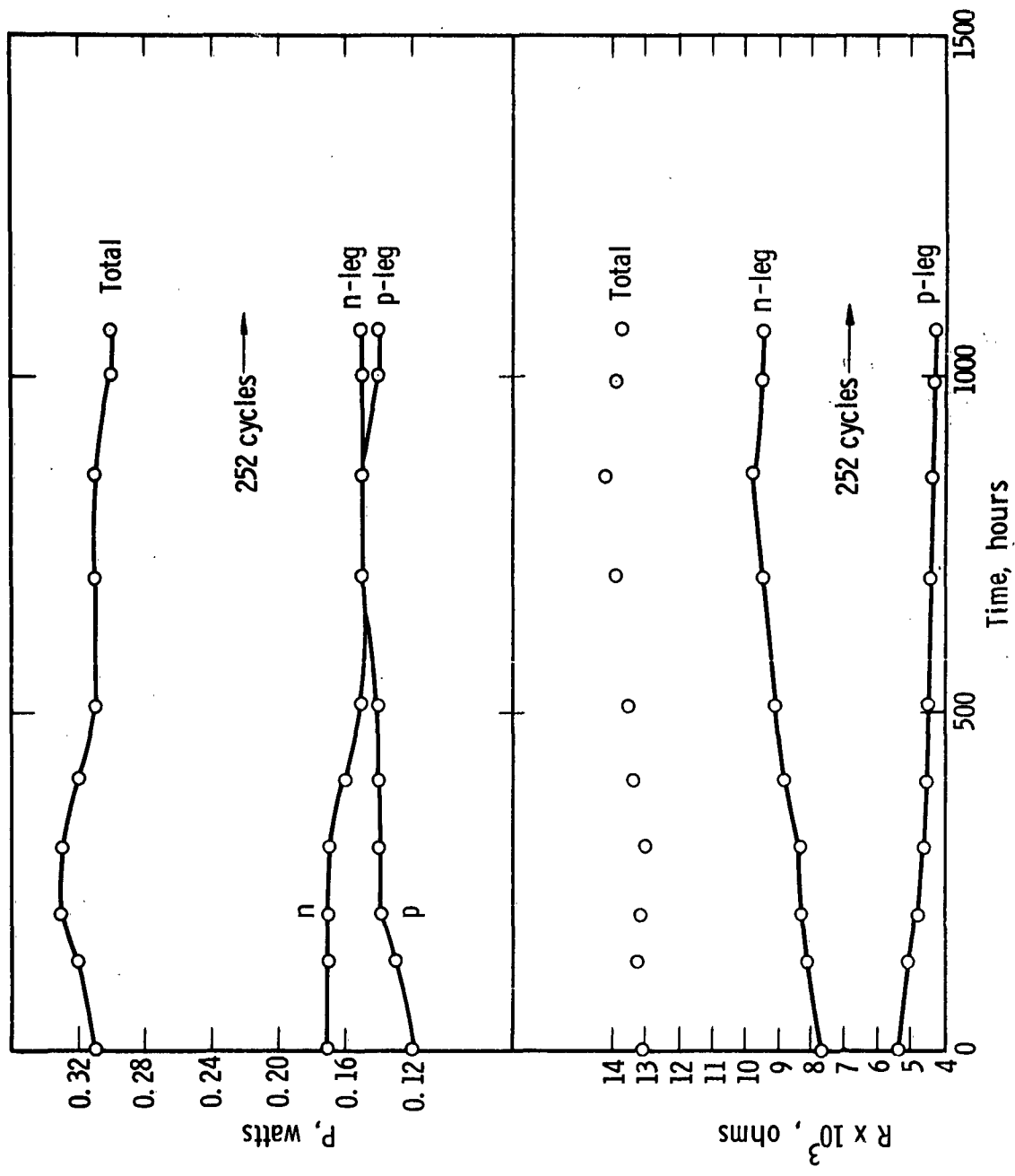Fig. 4—Thermoelectric properties of $Sb_{1.7}Bi_{0.3}Te_3$
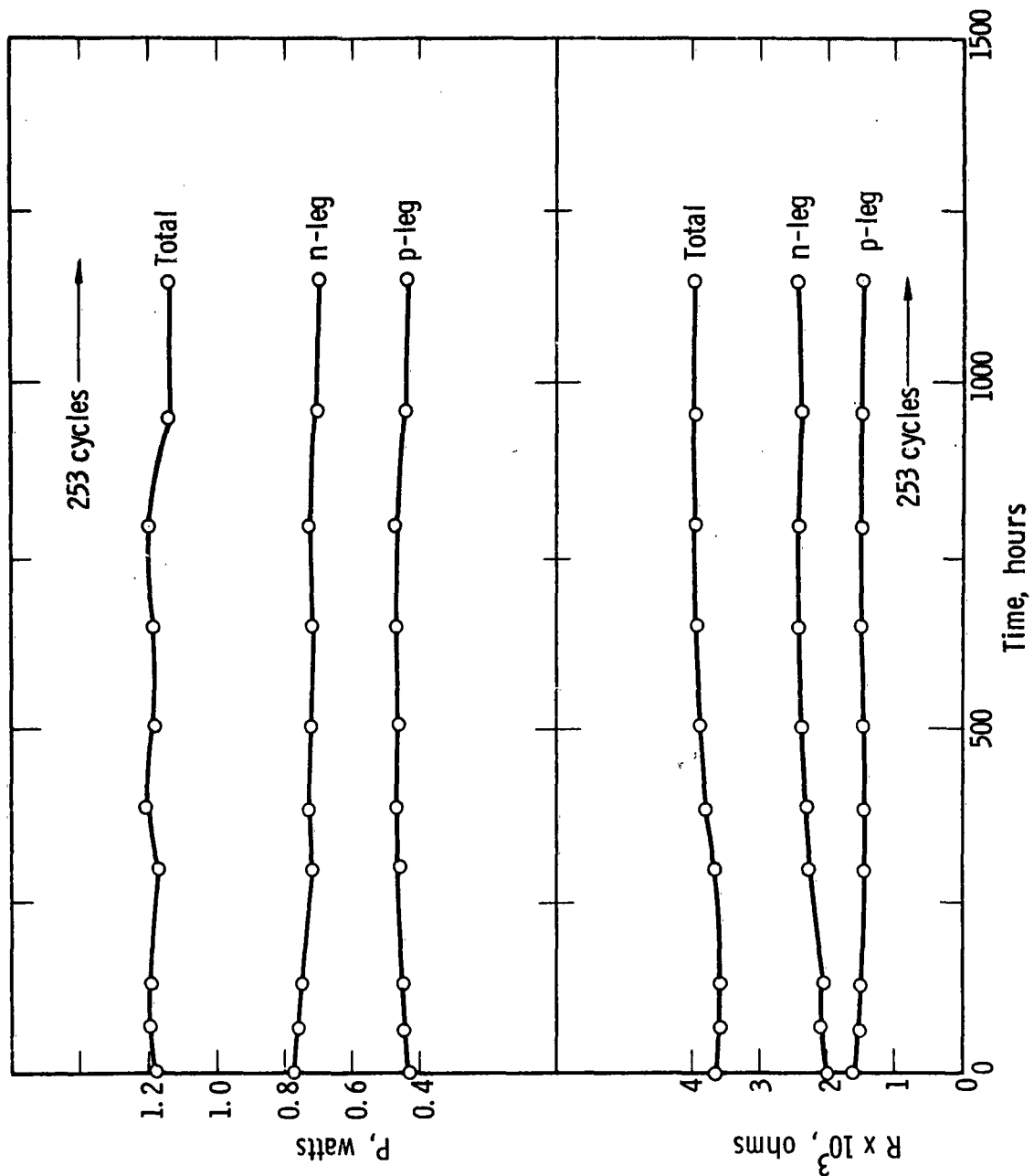
Fig. 5—Life test data; couple J-8
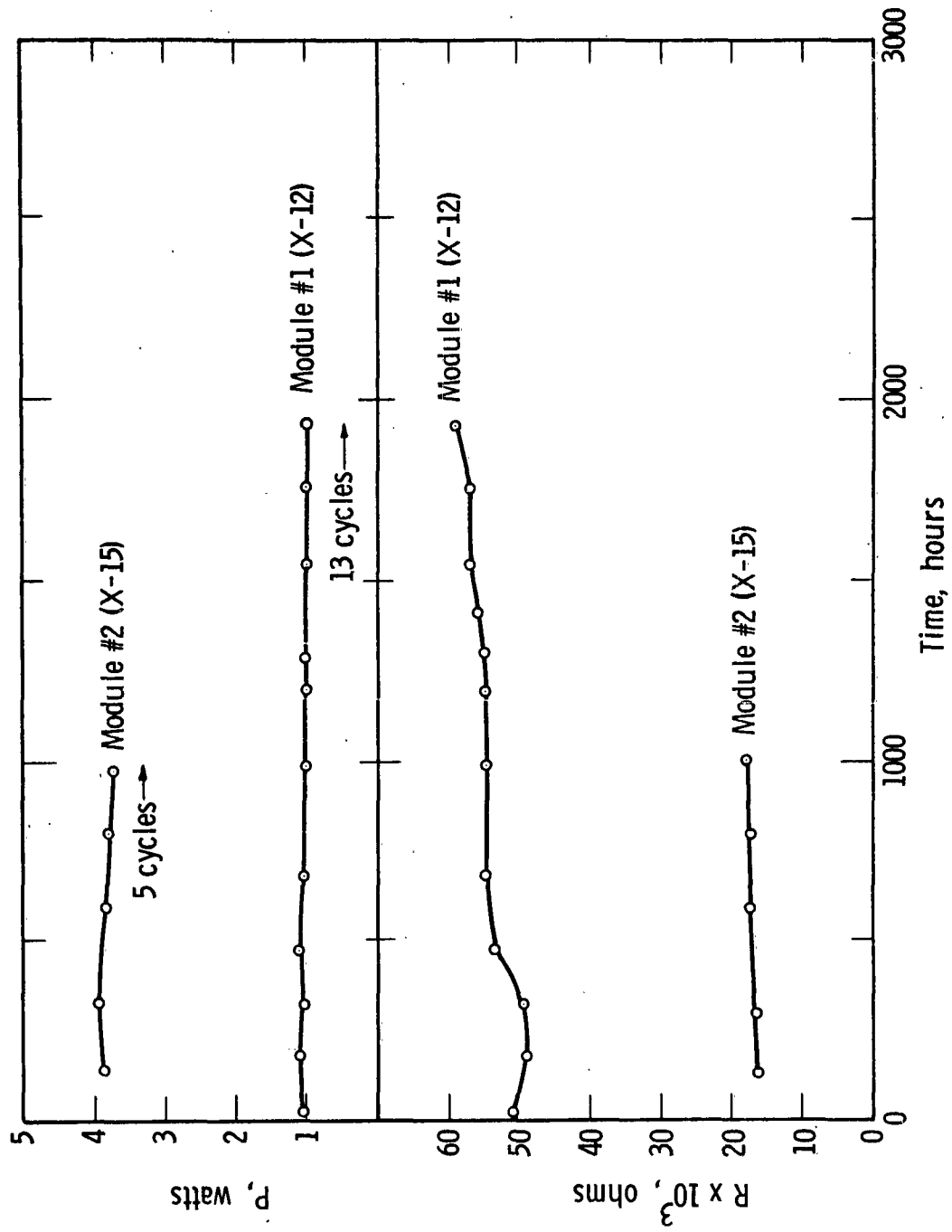
Fig. 6—Life test data, couple J-9

Fig. 7—Module test data

EQUIPMENT & SYSTEMS TECHNOLOGY

REPORT NO. 62-964-242-R2

THE PREPARATION AND EVALUATION OF INDIUM - ANTIMONY - TELLURIUM ALLOYS FOR THERMOELECTRIC POWER GENERATION

Synopsis

The thermoelectric properties of Sb_2Te_3 can be improved by alloying it with In_2Te_3, the best properties being found in the 5 to 10 mole percent In_2Te_3 range. Typical thermo-electric properties for the 5 mole percent In_2Te_3 composition are a Seebeck coefficient of + 184 $\mu V/°C$ and an electrical resistivity of 2.79 x 10^{-3} ohm-cm, both average values between 450 and 150°C, and a thermal conductivity of 0.0175 watts/cm-°C at room temperature. Pellets made from these alloys by powder metallurgy techniques are strong and are able to withstand rapid thermal cycling. Unfortunately, their high resistivity results in rather low power outputs. Preliminary life test results from thermocouples undergoing cycling and utilizing these materials as "p"-legs are encouraging. The indium-antimony-tell-urides must be operated in oxygen-free atmospheres as they have no oxidation resistance at 425°C, the normal hot-side temperature.

R. G. R. Johnson

July 18, 1962

I. Introduction

The goal of the program in which these alloys were developed was to find a "p"-material which could be fabricated into pellets that would operate without degradation due to thermal cycling. Such alloys exist in the In-Sb-Te ternary system along the line connecting the intermediate binary compounds Sb_2Te_3 and In_2Te_3. It was found that the thermoelectric properties of such In-Sb-Te alloys could be varied by changing composition along this line. Thermocouples using pellets made of an alloy in this system are currently being evaluated.

II. Conclusions

1). The most promising alloys lie between 5 and 10 mole percent In_2Te_3, the balance being Sb_2Te_3.

2). Over a 450-150°C ΔT, alloys within this compositional range are characterized by average Seebeck coefficients between +184 and +218 $\mu V/°C$ and average electrical resistivities between 2.79 and 6.15 x 10^{-3} ohm-cm.

3). The alloys within this range have room temperature thermal conductivities between 0.0175 and 0.0112 watts/cm-°C.

4). Alloying In_2Te_3 with Sb_2Te_3 drastically lowers the room temperature thermal conductivity of the latter compound.

5). The figure of merit values for these alloys are relatively low, probably less than 1 x $10^{-3}/°K$ over a 450-150°C ΔT.

6). Since the indium-antimony-tellurides are oriented materials, it is necessary to press pellets in rectangular form to preserve the orientation.

7). Cold pressed and sintered pellets were thermal cycled for 100 hours at a rate of one cycle per hour with a hot-side temperature of 450°C without any degradation of the electrical properties. No cracks were visible in the

microstructure of these cycled pellets.

8). Nicrobraz 10 or Fe can be plasma sprayed onto the ends of pellets to serve as barrier layers. If Fe is used, it must be overlaid with a thin plasma-sprayed layer of Ni for wetting purposes during joining.

9). Cu is a good match for the 5 mole percent In_2Te_3 alloys, which has a coefficient of thermal expansion of $15.7 \times 10^{-6}/°C$ between room temperature and 500°C.

10). Plasma-sprayed pellets can be joined to Cu straps with a Au-49 wt. percent In alloy which melts at 500°C.

11). Plain pellets can also be joined to a plasma-sprayed Ag-Nicrobraz 10 layer on a Cu strap at 575°C.

12). Thermocouples utilizing these pellets and joining techniques have been successfully operated for 1500 hours or more and up to 300 thermal cycles over a 425-100°C ΔT. When cycled couples failed, failure occurred at the hot-side joints and not in the pellets themselves.

13). Thermocouples utilizing indium-antimony-telluride pellets can not be operated in air due to the low oxidation resistance of these alloys.

14). The alloys of interest melt in the vicinity of 600°C.

Procedure

The indium-antimony-tellurium ternary system was first investigated using 100 gm tube heats. After calculations had been made, the individual elements (all at least 99.99 percent pure) were charged into 1/2-inch diameter Vycor tubes. Each tube was evacuated, sealed, and the contents melted at 825°C. After being mechanically agitated for one hour at the melting temperature to insure complete homogenization, tubes were cooled within the furnace until the melt solidified. Each cylindrical ingot, still within its Vycor tube, was then annealed for 8 hours at 475°C.

When the anneal had been completed, the ingots were sectioned transversely for testing. Room temperature properties were determined on 1/2-inch long pellets using Ga-In as a contacting agent where necessary. Large ΔT properties were also determined on 1/2-inch long pellets, but here a Bi-Sn-In contacting alloy was used since Ga will react with the indium-antimony-tellurides at elevated temperatures. Seebeck coefficients and electrical resistivities as a function of temperature were measured on 1-inch long pellets in an apparatus especially designed for this purpose. No contacting alloy was necessary here.

500 gm heats were next made in a Balzers furnace under an argon atmosphere by induction melting the correct proportions of the three elements together in a graphite crucible at 750°C. The melt was then cast onto a carbon-coated water-cooled copper mold. After hand crushing these chill cast ingots to -60 mesh powders in a steel mortar and pestle, rectangular pellets were cold pressed at 35 tsi in graphite-lubricated carbide-lined steel dies. Sintering took place in an argon atmosphere at 500°C for 3 hours. Once sintered

these pellets were tested in the same manner as the earlier cast pellets.

To determine their ability to withstand thermal cycling, plain 1/4-inch square x 1/2-inch long pellets without barrier layers were mounted upright between strips of graphite. One graphite strip was heated to 450°C, while the other was water cooled so as to maintain it at 150°C. Once every hour the row of pellets would be thermal cycled by simply turning the heater off for 15 minutes. Since the pellets were not bound to the graphite strips, this operation was known as unrestrained cycling.

Cu was chosen as the hot strap material for the argon tests and straps 3/4 x 3/8 x 0.07 inches were made. These straps were used for 1/4-inch square x 1/2-inch long pellets joined upon a 1/4-inch square face. Ni straps, 9/16 x 1/2 x 0.07 inches, were used for air tests, and where it was desired to join to the 1/2 x 1/4-inch faces of the pellets. Each strap had a thermocouple hole drilled into its long edge. One surface of the Cu straps was sandblasted and plasma sprayed with approximately 0.003 inches of Ni.

Two different joining procedures were used to build thermocouples. In the first, the side of the pellet to be joined to the hot strap was roughened on a precision sandblaster, cleaned with trichloroethylene, and plasma sprayed with an inert material (inert with respect to the pellet). The plasma-sprayed face of the pellet was placed upon the plasma-sprayed Ni side of the Cu strap with a 0.005 inch thick preform of the Au-In alloy between the two. A spring-loaded graphite jig was used to hold the components together. All components were cleaned and degreased prior to jigging. Argon-filled retorts, large enough to contain several graphite jigs, were used for joining.

Holding the jigged couples at 500°C for 15 minutes caused the Au-In to melt and flow and form the joint. It is advisable to paint the sides of the pellet immediately adjacent to the barrier layer with stop-off to prevent the Au-In alloy from flowing up onto the pellets during brazing. Since both the "p"-leg and the "n"-leg are joined simultaneously, this operation produces what is known as a one-step couple.

The other joining technique was a two-step method. That is, the two legs were joined separately. A powder mixture (20 wt. percent Ag, 80 wt. percent Nicrobraz 10) was plasma-sprayed on one-half of the hot strap. One surface of an indium-antimony-telluride pellet was polished, degreased and placed against the Ag-Nicrobraz 10 layer on the strap. At 575°C the pellet would react with the Ag-Nicrobraz 10 to produce a joint. A PbTe pellet could then be joined to the other half of the strap with the Au-In alloy as in the first technique.

Only the cold-side joints remained to be made. For this step the cold-side ends of the pellets were polished, degreased and ultrasonically wet with pure Sn. To perform this wetting, the couples were heated above the melting point of Sn on a hot plate (this can be done in air), and the bare ends of the legs were wiped across the tinned end of the ultrasonic gun. The couples were now returned to the hot plate while the Cu cold caps and braids were ultrasonically tinned and positioned on the pretinned legs. Once the Sn froze the couples were complete. Since the cold caps contain thermo-couple holes, it was found best to position the instrumentation thermocouples in the holes before tinning the caps to assure good thermal and electrical contact.

Completed couples utilizing all the plasma-spraying conditions and the direct joints to the Ag-Nicrobraz 10 layer were then life tested in an argon atmosphere using approximately a 425-100°C ΔT. After roughly 150 hours of steady state operation, the couples were thermal cycled at a rate of one cycle every three hours. After the accumulation of 300 cycles or 1000 hours, the couples were returned to steady state operation. At the present time some of the couples have run continuously for over 1500 hours. Some life tests in air were also attempted.

Two modules were built using one-step indium-antimony-telluride, lead telluride couples. The four couples in each module were connected in series and are currently being operated in an argon-hydrogen atmosphere.

Results and Discussion

The 100 gm heats, which were made in evacuated Vycor tubes, covered the Sb_2Te_3-In_2Te_3 system from pure Sb_2Te_3 to 66.7 mole percent In_2Te_3 including 10, 18, 25, 33.3, and 50 mole percent In_2Te_3 compositions in addition to the aforementioned alloys. Other intermetallics from the In-Te binary system, such as InTe and In_2Te_5, were also tried in combination with Sb_2Te_3, but none looked as good as the Sb_2Te_3-In_2Te_3 alloys. Actual weight percentages of the three elements are to be found in Exhibit 1.

As can be seen from Exhibit 2, where the electrical properties are plotted as a function of the In_2Te_3 composition, the room temperature Seebeck coefficient (solid line) reaches a positive maximum around 30 mole percent In_2Te_3, then falls off rapidly until somewhere over 60 mole percent In_2Te_3

the system goes "n"-type. However, the average Seebeck coefficient ($\bar{\alpha}$)
between 450 and 150°C (dashed line), reaches its positive maximum sooner --
around 20 mole percent In_2Te_3. Between 0 and 66.7 mole percent In_2Te_3,
the room temperature electrical resistivity increases rapidly with increas-
ing percentages of In_2Te_3. The 450-150°C average resistivity ($\bar{\rho}$) would
be indistinguishable from the room temperature resistivity on the scale
used, so only the latter is plotted. When the $\bar{\alpha}^2/\bar{\rho}$ ratio is computed for
the 100 gm tube heats as in Exhibit 1, the best alloy is seen to lie at 10
mole percent In_2Te_3.

Exhibit 3 shows the large effect that In_2Te_3 additions have upon
the total thermal conductivity of Sb_2Te_3 - decreasing it rapidly up to about
25 mole percent In_2Te_3 where it is roughly only one-fifth that of pure Sb_2Te_3.

On the basis of the tube heat data, three 500 gm heats containing
5, 10, and 15 mole percent In_2Te_3 were chill cast in the Balzers furnace.
Later, heats containing 6 and 7 mole percent In_2Te_3 were also made. All
these heats were crushed to -60 mesh powder, and rectangular pellets,
1/4-inch square x 1/2-inch long, were cold pressed at 35 tsi and sintered
at 500°C for 3 hours. Since the indium-antimony-tellurides in this compos-
itional range are oriented materials, it is necessary to use rectangular
pellets, where the pressing direction is perpendicular to the intended cur-
rent path. The 1/4-inch square x 1/2-inch long pellet size was chosen since
this makes the length to diameter (here the diagonal) ratio greater than 1.33,
a necessary condition for minimizing the doming stresses set up when a Δ T
is imposed across the pellet. However, this geometry reduces the power

producing capability of the thermocouple - the price that must be paid for lessening the stresses set up in the hot-side joint during operation.

Data from the Balzers heats appears in Exhibit 1. In addition data points for the average 450-150°C ΔT Seebeck coefficients and room temperature thermal conductivities are plotted in Exhibits 2 and 3, respectively, as triangles. On the basis of α^2/ρ calculations, the 5 mole percent In_2Te_3 composition (Heat 3384) was chosen as the material for the "p"-leg of a thermocouple. Plots of α and ρ as a function of temperature are presented in Exhibit 4.

In the compositional range between 5 and 10 mole percent In_2Te_3, the indium-antimony-tellurides are soft materials which are able to withstand rapid thermal cycling as is shown by the data collected from the unrestrained cycling tests. In this test the pellets are mounted between two graphite strips, one of which serves as the 450°C hot side, the other as the 150°C cold side. The pellets are cycled once every hour. One-half of the pellets being cycled were examined after 11 cycles, the other half after 99 cycles. Data presented in Exhibit 1 shows no apparent degradation in either case. Nor were any cracks discernible in the microstructures of the cycled pellets.

Indium-antimony-telluride pellets were readily fabricated into thermocouple legs. Pellets were plasma sprayed on one 1/4-inch square face with approximately 0.003 inches of each of the following materials: Nicrobraz 10, Co, Fe, Cr, Ta and 310 SS. To aid in wetting during joining all the metallic layers were overlaid with a very thin plasma-sprayed layer of Ni.

An excellent low resistance joint could be made between the pellet and the strap with the Au-49 wt. percent In alloy. A thin layer of Ni plasma sprayed over the Cu strap prevented excessive reaction between the Au-In and the Cu during joining. Cu was chosen for straps since its coefficient of thermal expansion closely matches that of the 5 mole percent In_2Te_3 alloy (Exhibit 5). PbTe pellets, plasma sprayed with Co and a Ni overlay, were used for the "n"-legs.

Of all such couples tested, only the ones with Fe and Nicrobraz 10 barrier layers proved successful. Two couples with plasma-sprayed Fe are presently on test. One of these utilizes 32,000 circular mil Cu braids on the cold side. This couple, known as RJ-12, has been operated in argon for 1600 hours and was thermal cycled at a rate of 1 cycle every 3 hours, accumulating a total of 298 thermal cycles. All the single couples discussed herein have been tested over a 300 to 340°C ΔT with the hot sides at 425°C.

Couple RJ-12 produced 0.27 watts at the start (after the couple had come to equilibrium), of which the "p"-leg contributed 0.10 watts and the "n"-leg 0.18 watts. Total power output (P_T) in watts was calculated from the relationship $P_T = E_o^2/4R$, where E_o is the open circuit voltage and R is the operating couple resistance. Likewise, the power outputs of the individual legs were also calculated from this relationship using the operating resistance of each leg. But here the open circuit voltage for each leg must be corrected to compensate for the voltage produced by the Seebeck effect of the potentiometer leads, which in this case are alumel thermocouple wires. No E_o correction is necessary when calculating

total power since, due to the circuitry, the two lead wire voltages are opposing and cancel each other.

After 1600 hours and 298 thermal cycles, couple RJ-12 was producing 0.26 watts, and it showed only a 4.6 percent increase in operating resistance. Individual leg power outputs have not changed. The "p"-leg resistance increased less than one percent, while the "n"-leg increased 4.4 percent. Most of this degradation occurred during the first 400 hours as can be seen in Exhibit 5. After 400 hours there was no further increase in resistance, and after 1052 hours, when cycling was discontinued, the resistance decreased.

Couple RJ-20, another two-leg thermocouple utilizing plasma-sprayed Fe and Co as barrier layers on the "p"-leg and "n"-leg respectively, is similar to couple RJ-12 except that the cold-side braid cross-section was reduced to 4,000 circular mils. The thinner braid had the effect of a thermal resistor, raising the average cold-side temperatures which in turn lowered the operating ΔT. Thus this couple produced less power than the preceeding one. The power was also reduced by higher operating resistances, which resulted from the higher cold-side temperatures (note the shape of the resistivity curves in Exhibit 4).

After 71 hours of operation couple RJ-20 had a power output of 0.20 watts total, of which 0.07 watts were contributed by the "p"-leg and 0.14 watts by the "n"-leg. After 1053 hours and 275 thermal cycles this couple had a total power output of 0.19 watts - 0.06 watts from the "p"-leg and 0.14 watts from the "n"-leg. During this time the total operating resistance has increased 11.9 percent, while the "p"-leg and the

"n"-leg have increased their respective resistances by 12.2 and 10.4 percent. As can be seen from Exhibit 7, the resistance of this couple has increased continuously during its operation. However, consideration should be given to the decrease in the ΔT across the "p"-leg since the start of the test. This shrinking ΔT could account for the decline in the power output. Note from Exhibit 7 that the increase in the "n"-leg ΔT after 800 hours produced a corresponding increase in the power output of this leg. The effect of discontinuing thermal cycling remains to be seen.

Another two-leg couple that has performed well is one that has plasma-sprayed Nicrobraz 10 as a barrier layer on one 1/4-inch square face of the "p"-leg, while the "n"-leg has a conventional layer of plasma-sprayed Co. Both legs were joined to the hot strap with Au-In brazing alloy. The story of this couple, identified as RJ-18, is clouded by the fact that after only 69 hours of operation it was removed from test to replace the cold side chromel-alumel thermocouples. After this operation the "p"-leg resistance rose 11.7 percent (Exhibit 8). Since this time the "p"-leg resistance has increased an additional 7.3 percent, while the "n"-leg resistance has not changed. This couple has now been operated 1233 hours and been thermal cycled 282 times.

Couple RJ-13 is different in that it uses no barrier layers. It is a single leg couple which has had one 1/4-inch square end of an indium-antimony-telluride pellet joined directly to a plasma-sprayed Ag-Nicrobraz 10 layer on a Cu strap. This joint is mechanically strong, but it has unusual effects upon the electrical properties of the pellet. First, the starting operating resistance was 7.92×10^{-3} ohms, almost 1×10^{-3} ohms

below the expected value. Second, the Seebeck coefficient was lower than expected. Exhibit 9 shows that the resistance decreased until cycling began, after which it generally increased until 435 hours had elapsed at which time the couple was removed from test to replace the cold-side chromel-alumel thermocouple. When testing was resumed, the resistance had dropped to a value lower than any previously recorded - an effect attributed to the inaccurate readings obtained before the indicating thermocouple was changed. From this point on until 1054 hours and 309 cycles had been accumulated the resistance gradually increased until it reached its initial starting value. Shortly after the couple had been returned to steady state operation, the resistance began increasing rapidly. After 1438 hours the couple was removed from test, and it was found that the leg had separated from the strap at the hot-side joint. During the test period the average Seebeck coefficient declined from an initial value of 180 μV/°C to a final value of 160 μV/°C. The initial decrease in resistance and the gradual decline of the Seebeck coefficient during the duration of the test were attributed to a gradual doping of the pellet by Ag from the plasma-sprayed layer on the strap, while the resistance increase during cycling was caused by a gradual yielding of the hot-side joint. Incidentally, the 5 mole percent In_2Te_3 alloy will not join directly to plain Nicrobraz 10; the Ag is a necessary component.

The fifth and final couple to be considered is RJ-26, a two-step, two-leg, direct joint couple using indium-antimony-telluride and lead telluride. This couple is unique in that both pellets were joined on a 1/2 x 1/4-inch face, and in that the lead telluride has been joined directly to a Ni hot strap at 690°C without benefit of barrier layers or joining alloys.

The Ni strap was chosen because of good oxidation resistance for air tests (which were all unsuccessful owing to the extremely rapid oxidation of the indium-antimony-telluride pellets in air at 425°C). For the "p"-leg joint, the Ag-Nicrobraz 10 mixture was plasma sprayed onto the Ni strap, and the joint made in the usual manner at 575°C.

Theoretically, this couple should have four times the power output of the previously described couples, since the resistance of the couple has been quartered by turning the pellets on their "sides" (the current path here is still perpendicular to the pressing direction). Such quadrupling of the power output was not achieved, however. At equilibrium the best power output recorded was 0.96 watts instead of the expected 1.08 watts, even though the total resistance was more than quartered. The low initial power output was due to a substantial lowering of the Seebeck coefficients as a result of the joining techniques. Exhibit 10 shows that the operating resistance of the "p"-leg has remained essentially unchanged since the start of the test, while that of the "n"-leg has increased appreciable, especially during cycling. However, the power output of the "p"-leg has decreased 37.5 percent, owing to a 30 μV/°C decrease in the average Seebeck coefficient during the test. It appears that the Ag-Nicrobraz 10 joining procedure can not be used on indium-antimony-telluride due to the adverse effect upon the electrical properties of the pellet, even though such a joint is mechanically sound. The direct joint between PbTe and Ni is of no interest because of its lack of resistance to thermal cycling.

As a summary Exhibit 13 describes in tabular form the five couples discussed in the report.

As has been mentioned before, pellets made from the 5 mole percent In_2Te_3 alloy will not operate in air at 425°C. At this temperature the pellet will oxidize at the pellet-barrier layer interface or at the pellet-Ag-Nicrobraz 10 junction in the case of the direct joint. Oxidation is rapid, and within 24 hours the pellet will separate from the hot strap. Coating the hot junction with Sauereisen 29 had no effect. A vacuum-impregnated coat of sicon-aluminum would extend the life of the couple in air by only about 24 hours. It is not believed that the other alloys in this system will show any better oxidation resistance.

Two four couple modules using duplicate RJ-20 couples have been built and are presently being tested. Both modules are performing so far in a manner similar to that of the single couple. Each has slightly over four times the power output of the single couple, which is the result of a larger Δ T. Cycling is proceeding at a rate of one cycle per hundred hours of operation. Exhibits 11 and 12 present the life test data in graphical form.

In general, the indium-antimony-tellurides, which are typified by the 5 mole percent In_2Te_3 alloy, possess good mechanical properties but low thermoelectric efficiencies. Their low efficiencies result from high electrical resistivities, which in turn limit their power outputs. Because of their anisotropy, pellets must be pressed in rectangular shapes so that the current path will be perpendicular to the pressing direction, this being the direction of easy electrical conduction. Such a pressing requirement precludes the use of pressed metallic caps to serve as barrier layers. However, an effective barrier layer can be applied by plasma spraying a

roughened surface of the pellet with Fe or Nicrobraz 10. Cold side caps and braids can be readily joined to pellets which have been ultrasonically prewet with pure Sn.

These pellets have shown their ability to withstand high thermal cycling rates without cracking. If sound strong joints can be made, these pellets can be used in thermocouples with low degradation during operation. In certain sealed, inert atmosphere generator applications, where reliability and not the utmost in efficiency is the requirement, thermocouples with indium-antimony-telluride "p"-legs may find application.

Acknowledgement:

EXHIBIT 1. Compositions and Thermoelectric Data and Unrestrained Cycling Results

Alloy No.	Type of Heat	Percent In_2Te_3	Weight Percents In	Sb	Te	α, $\mu V/°C$ at 30°C	$\rho \times 10^3$, Ω-cm at 30°C	K, watts/cm-°C at 30°C	$\bar{\alpha}$, $\mu V/°C$, 450-150°C	$\bar{\rho} \times 10^3$, Ω-cm 450-150°C	$\bar{\alpha}^2/\bar{\rho}$ $\times 10^5$
94	Tube	0	0	38.88	61.12	64	0.21	0.0449	121	0.61	2.40
75	Tube	10	3.67	35.07	61.26	97	1.80	0.0152	203	3.36	1.23
76	Tube	18	6.62	32.01	61.37	134	5.32	0.0094	217	6.73	0.70
59	Tube	25	9.21	29.32	61.47	181	15.6	0.0083	208	9.92	0.44
10	Tube	33.3	12.31	26.11	61.58	201	31.9	0.0083	187	15.5	0.23
60	Tube	50	18.53	19.66	61.81	149	173.0				
61	Tube	66.7	24.80	13.16	62.04	-62	621.0				
3384	Balzers	5	1.84	36.98	61.18		1.20	0.0175	184	2.79	1.21
3421	Balzers	6	2.20	36.60	61.20			0.0159	196	3.54	1.09
3423	Balzers	7	2.57	36.21	61.22			0.0153	189	2.95	1.21
3386	Balzers	10	3.67	35.07	61.26			0.0112	218	6.15	0.77
3390	Balzers	15	5.52	33.16	61.32			0.0107	215	6.52	0.71

Alloy No.	Uncycled		11 Cycles		99 Cycles	
	$\bar{\alpha}$, 450-150°C	$\bar{\rho}$, 450-150°C	$\bar{\alpha}$, 450-150°C	$\bar{\rho}$, 450-150°C	$\bar{\alpha}$, 450-150°C	$\bar{\rho}$, 450-150°C
3384	184	2.79	179	2.52	179	2.74
3386	218	6.15	218	5.98	218	6.20
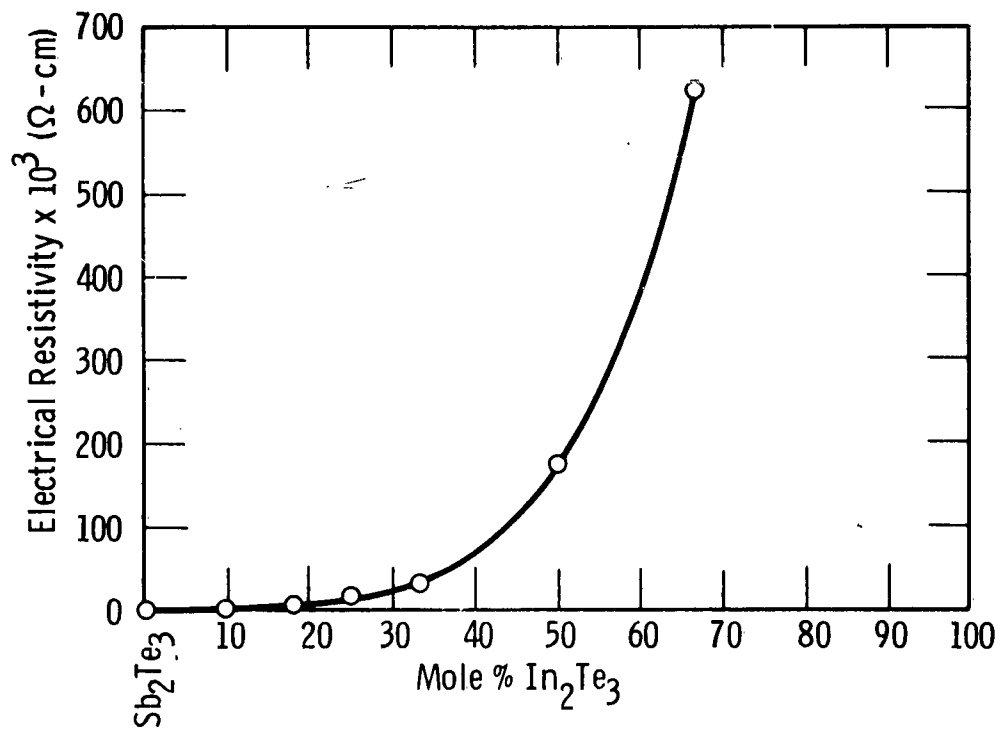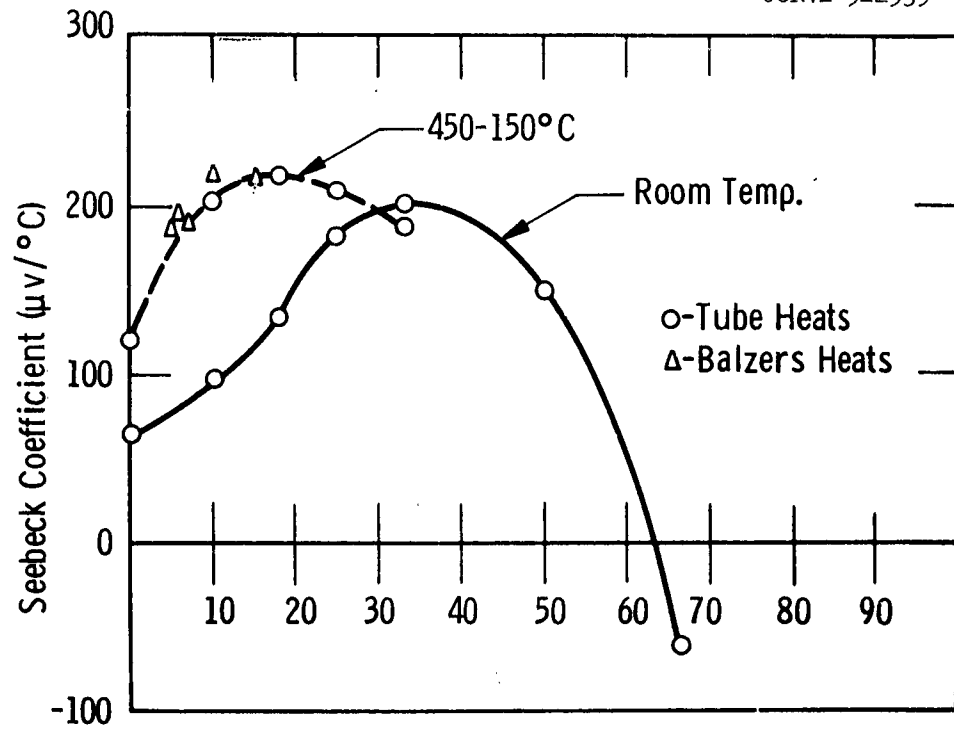
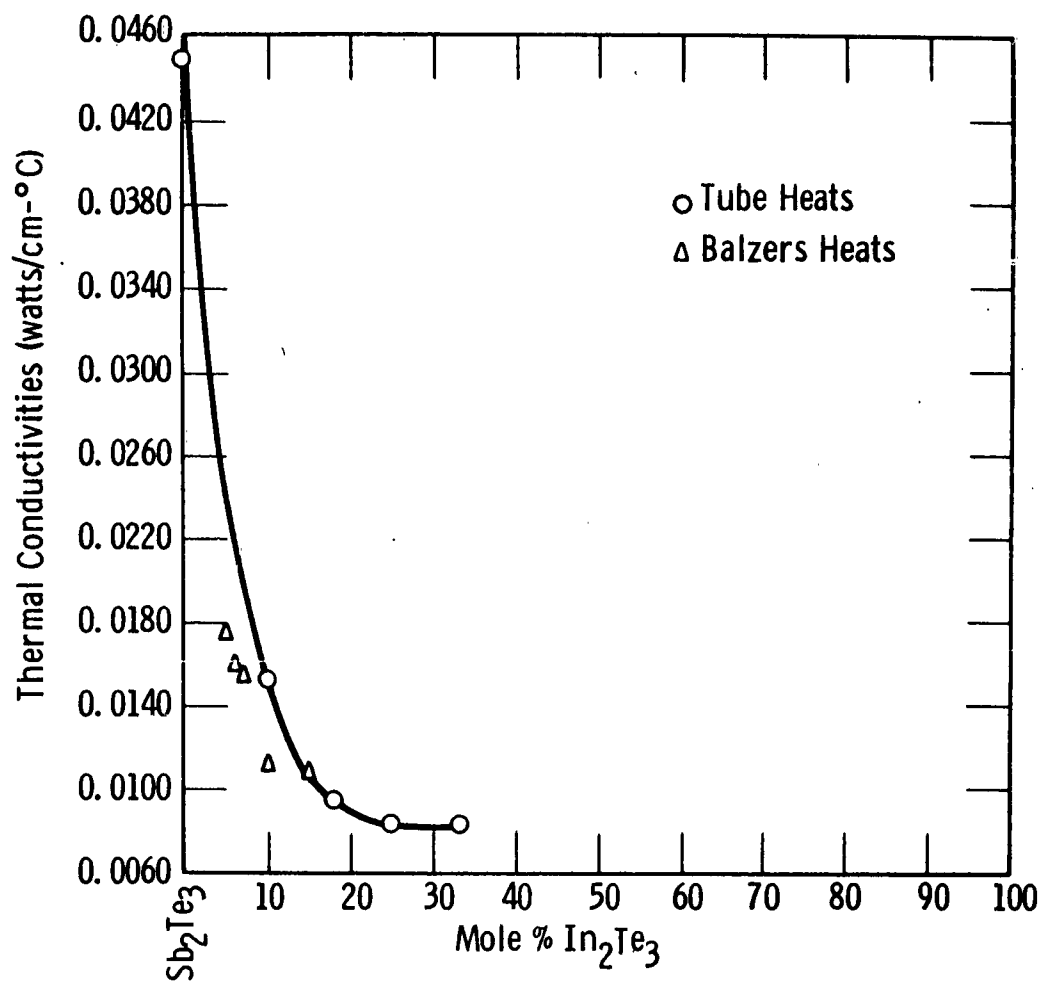Electrical properties of the Sb_2Te_3-In_2Te_3 system

EXHIBIT 2
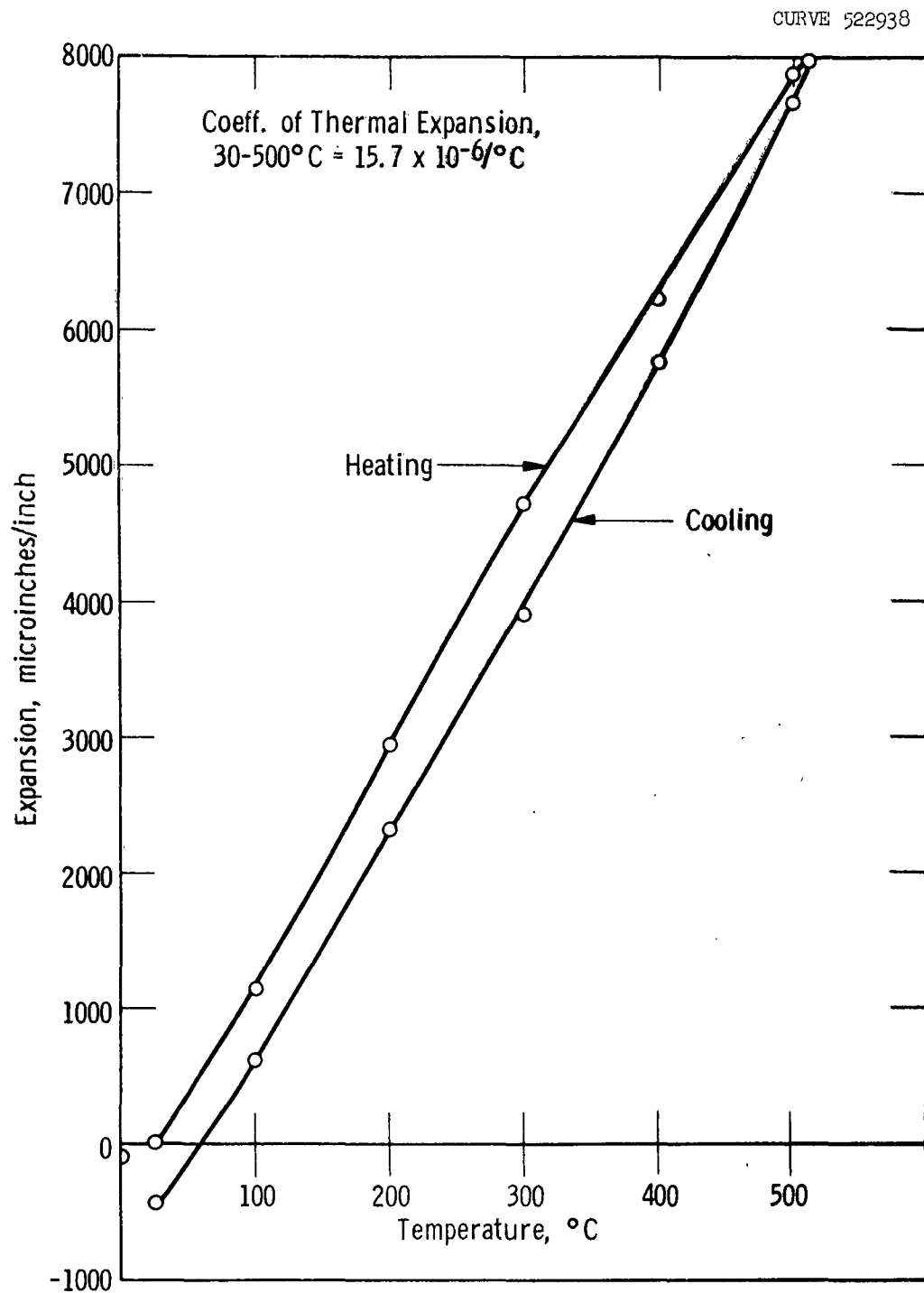
Room temperature thermal conductivities of the
Sb_2Te_3 - In_2Te_3 system

EXHIBIT 3
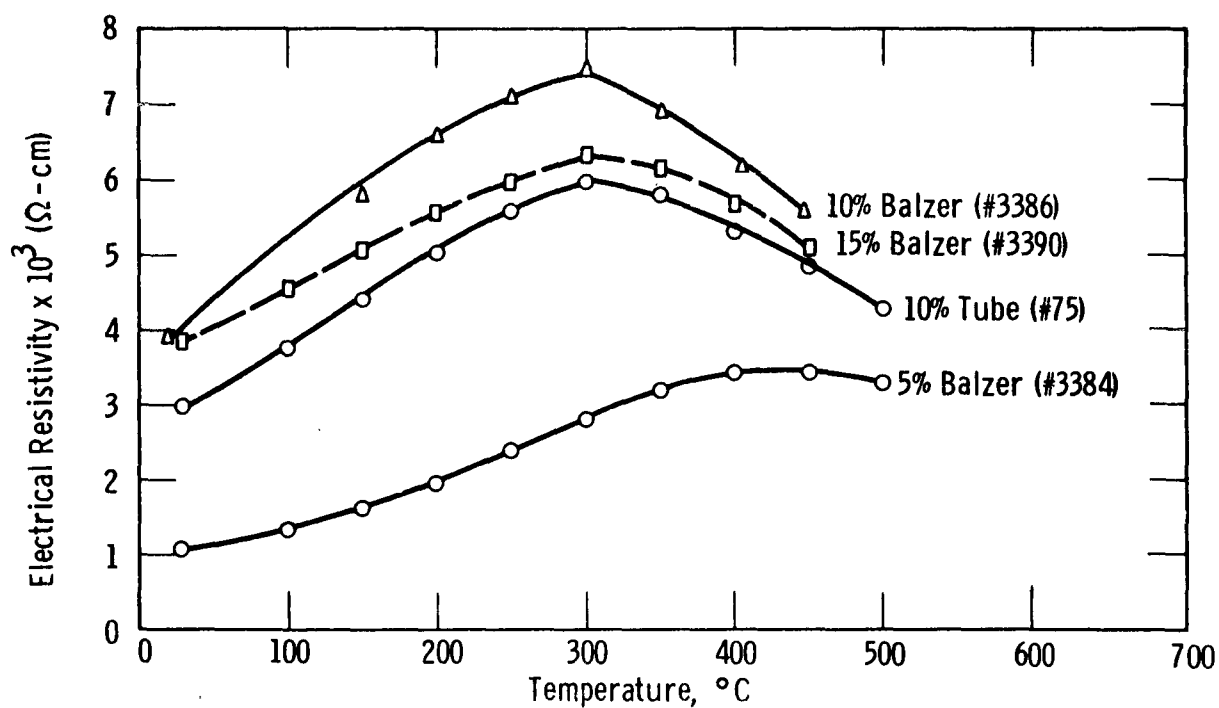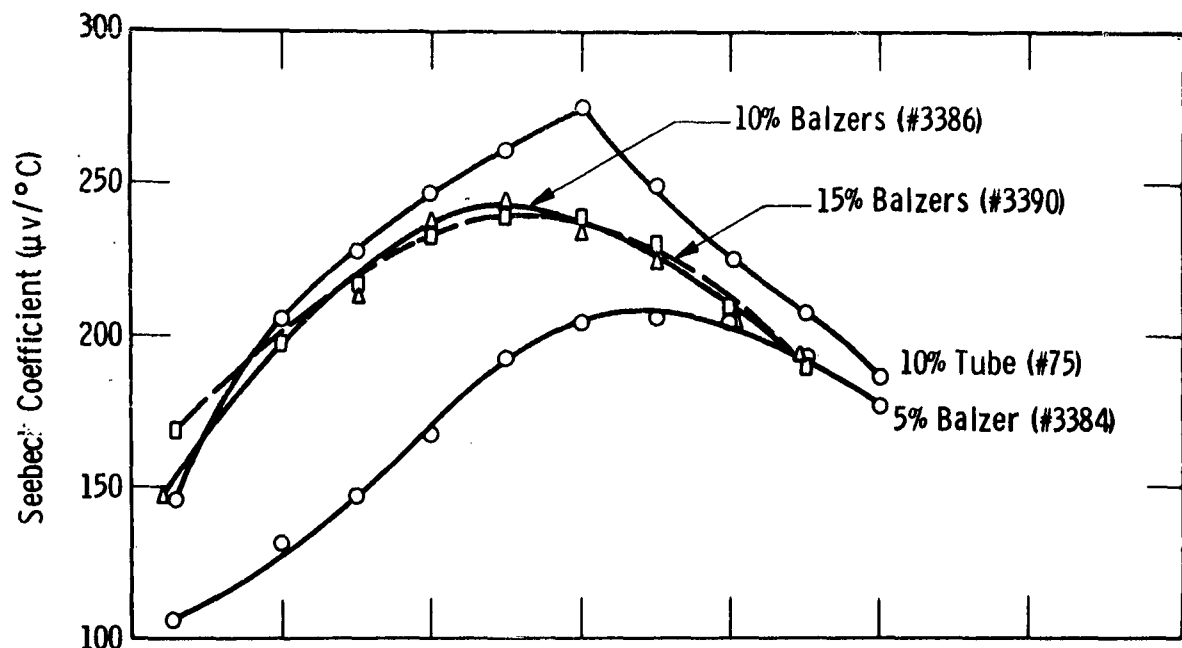
Seebeck coefficients and electrical resistivities vs. temperature
Percentages refer to % In$_2$Te$_3$

EXHIBIT 4

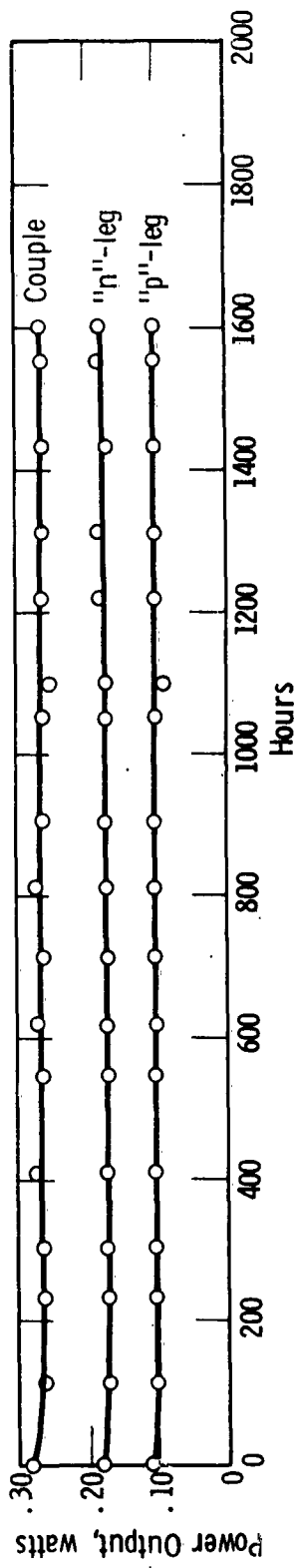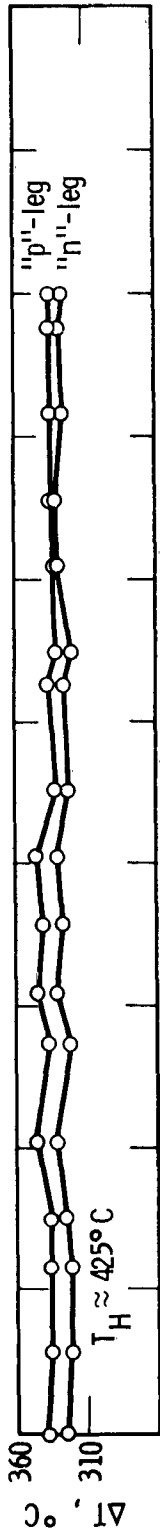Thermal expansion of Sb_2Te_3 - 5% In_2Te_3 (#3384)

EXHIBIT 5

CUDE 522733

298 Thermal Cycles
○ Couple

"p"-leg
"n"-leg

Resistance, Internal, milliohms

"p"-leg
"n"-leg

$T_H \approx 425°C$

ΔT, °C

Couple
"n"-leg
"p"-leg

Power Output, watts

Hours
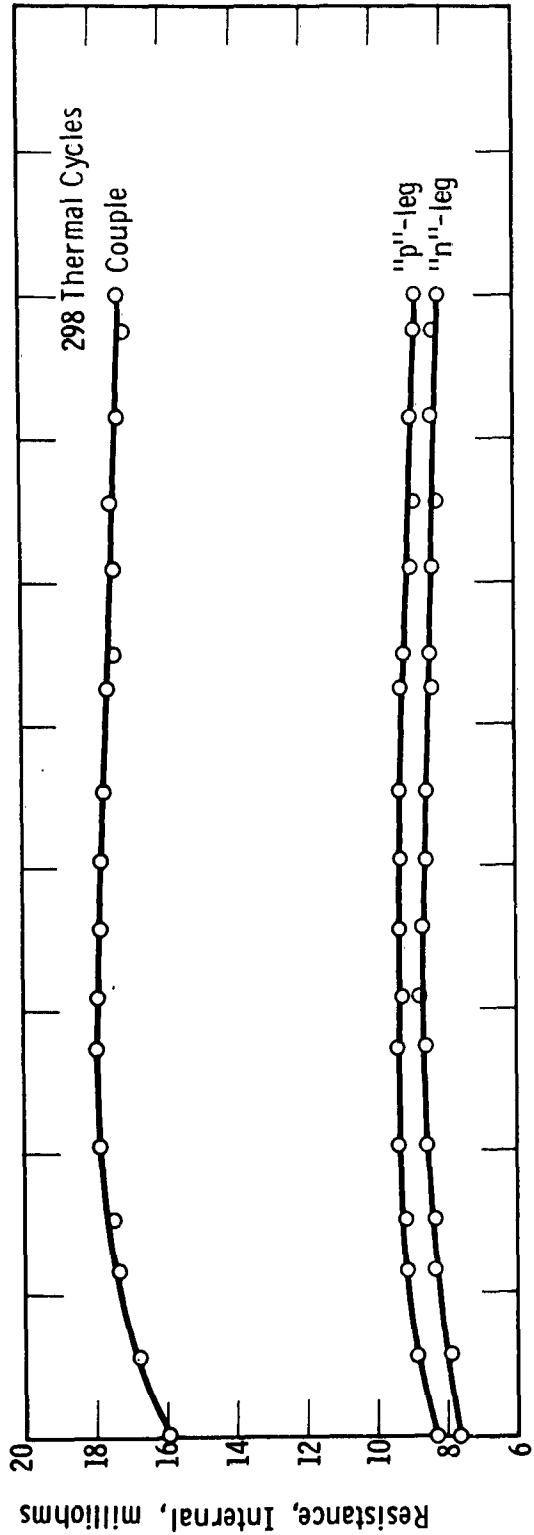
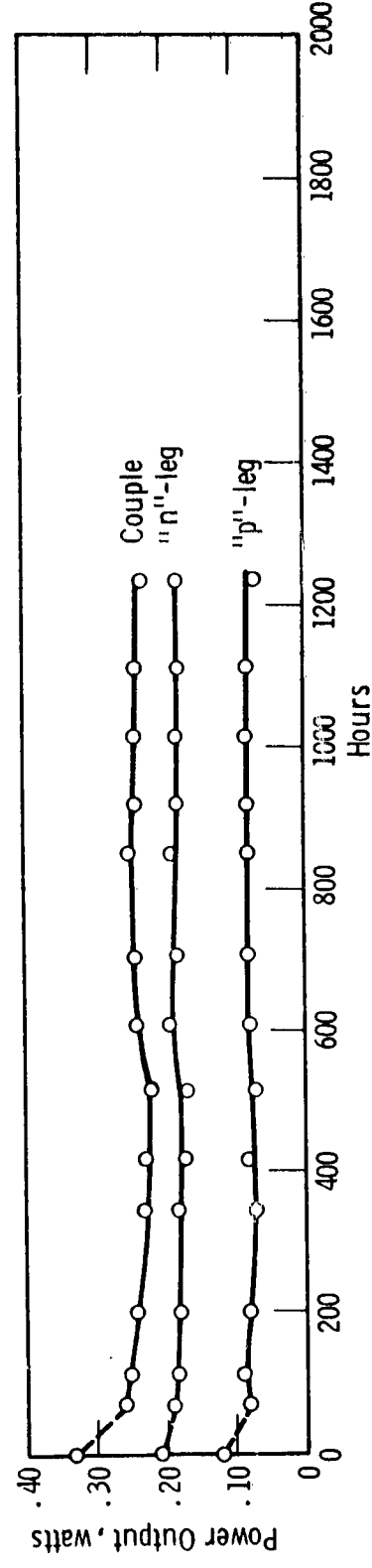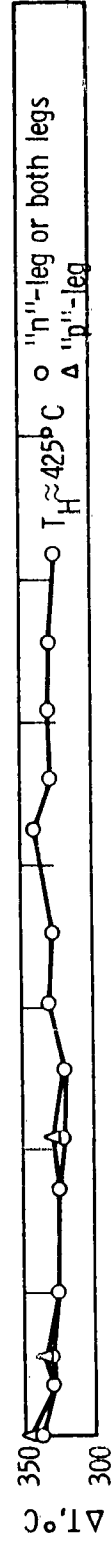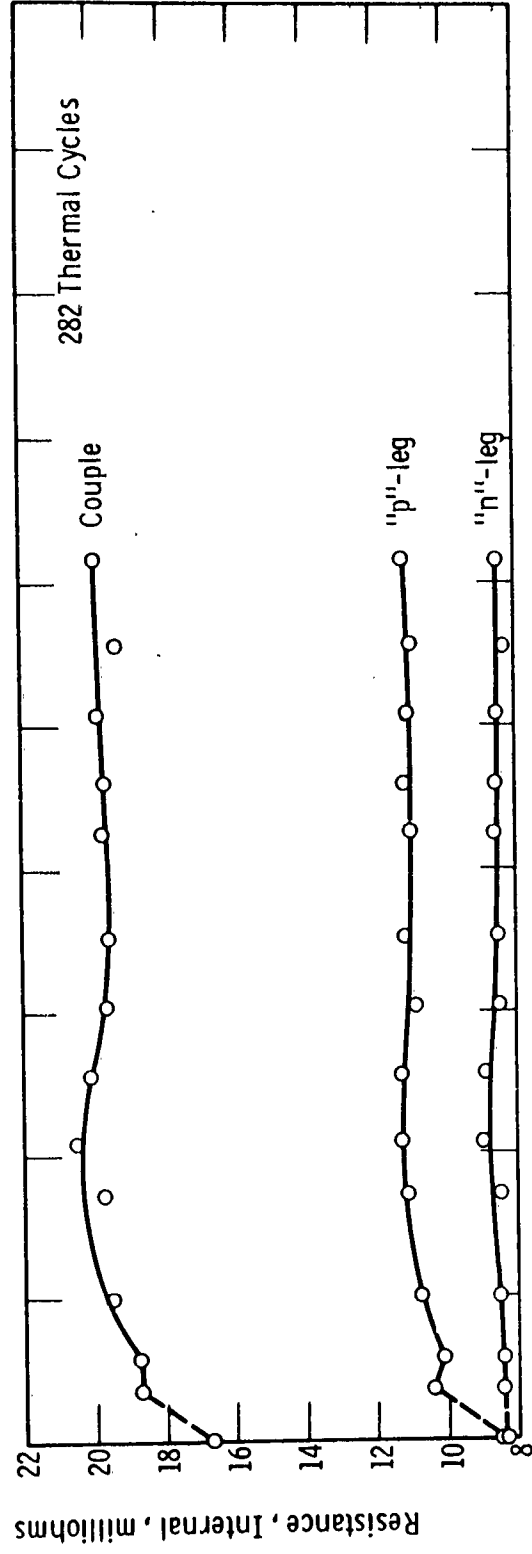Couple RJ-12, Argon atmosphere
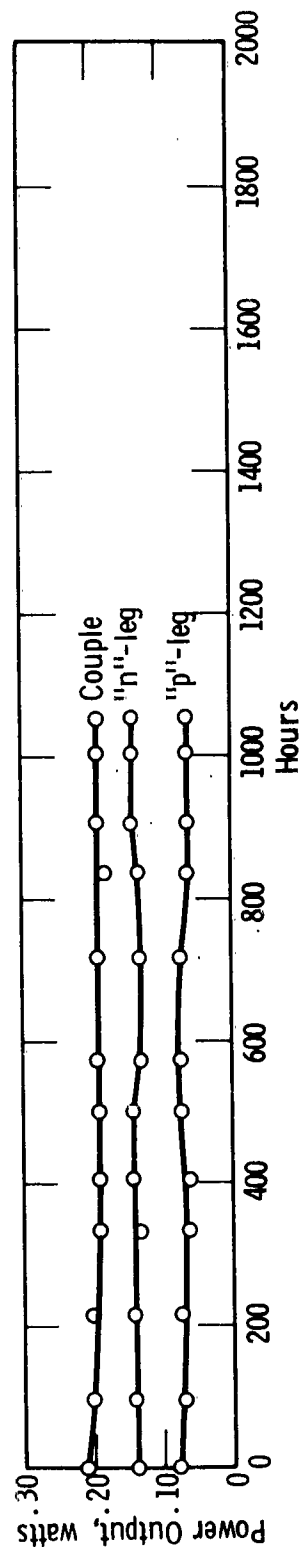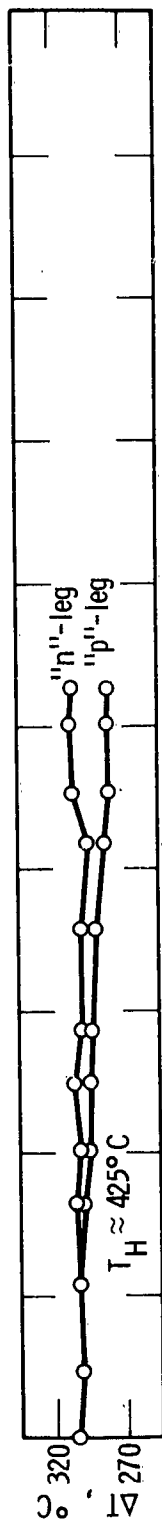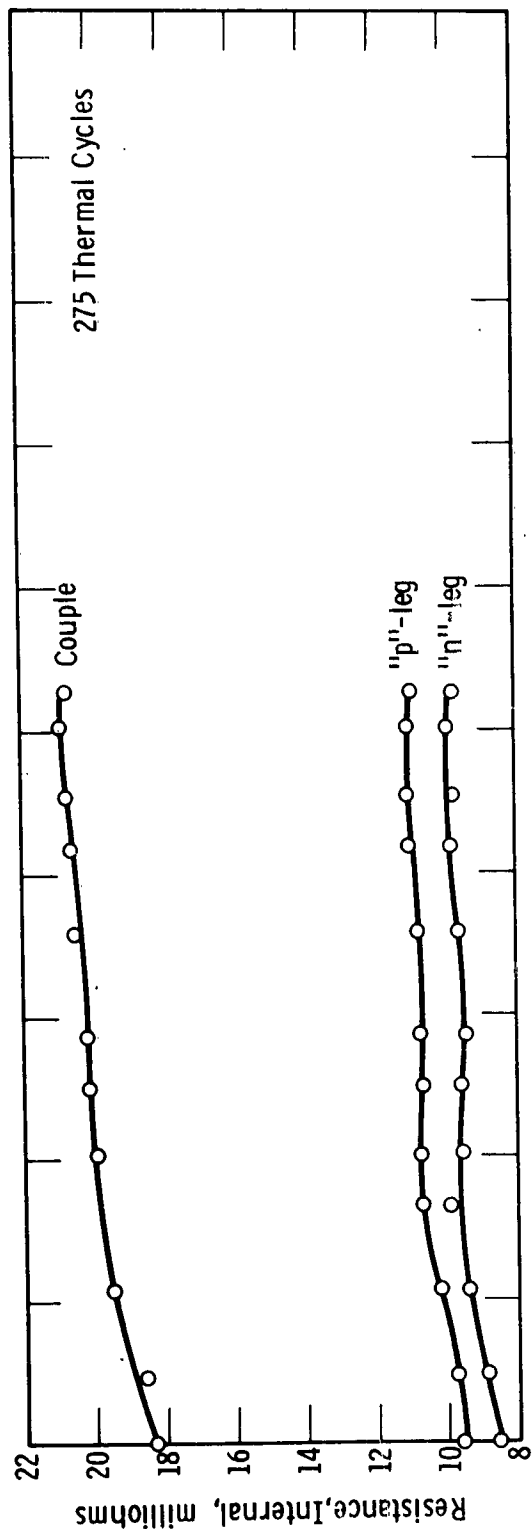
EXHIBIT 6

Couple RJ-20, Argon atmosphere

EXHIBIT 7

Couple RJ-18, Argon atmosphere

EXHIBIT 8

CURVE 522942

309 Thermal Cycles

$T_H \approx 425°C$

"p"-leg only

Resistance, Internal, milliohms

$\triangle T$, °C

Power Output, watts

Hours
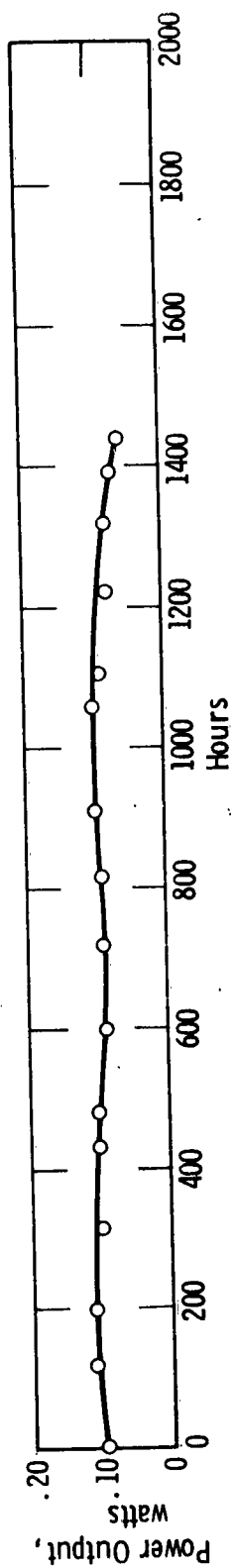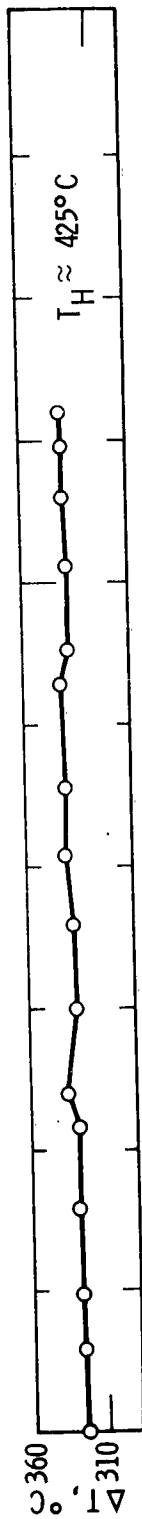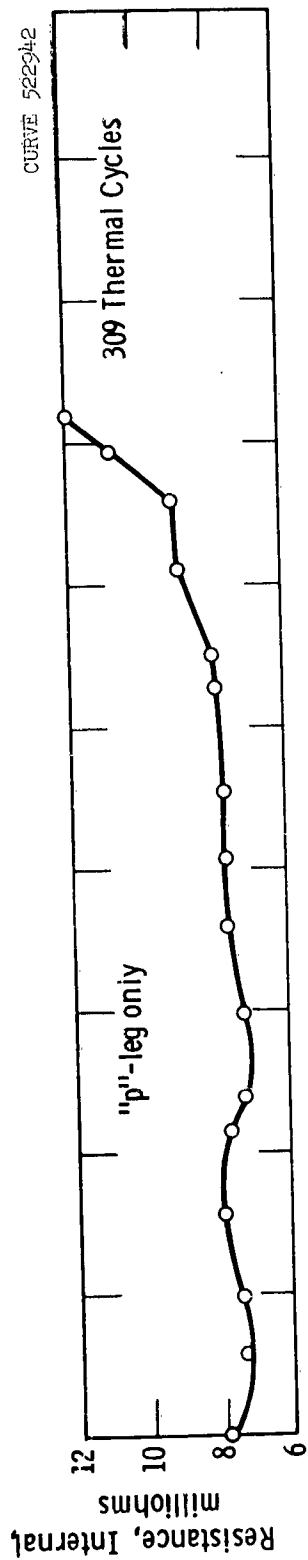
Couple RJ-13, Argon atmosphere

EXHIBIT 9

CURVE 522943

9 Thermal Cycles

Couple
"n"-leg
"p"-leg

Resistance, Internal, milliohms

$T_H \approx 425°C$

"p"-leg
"n"-leg

ΔT, °C

Couple

"n"-leg

"p"-leg

Power Output, watts

Hours
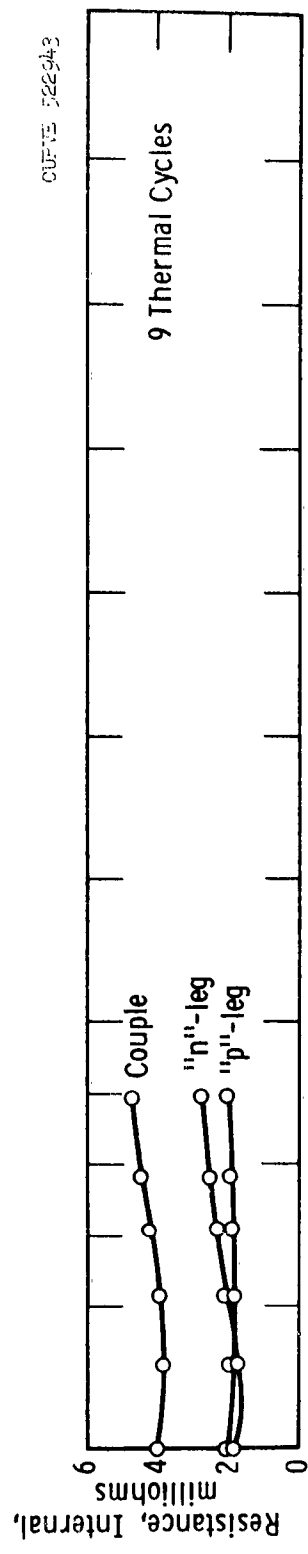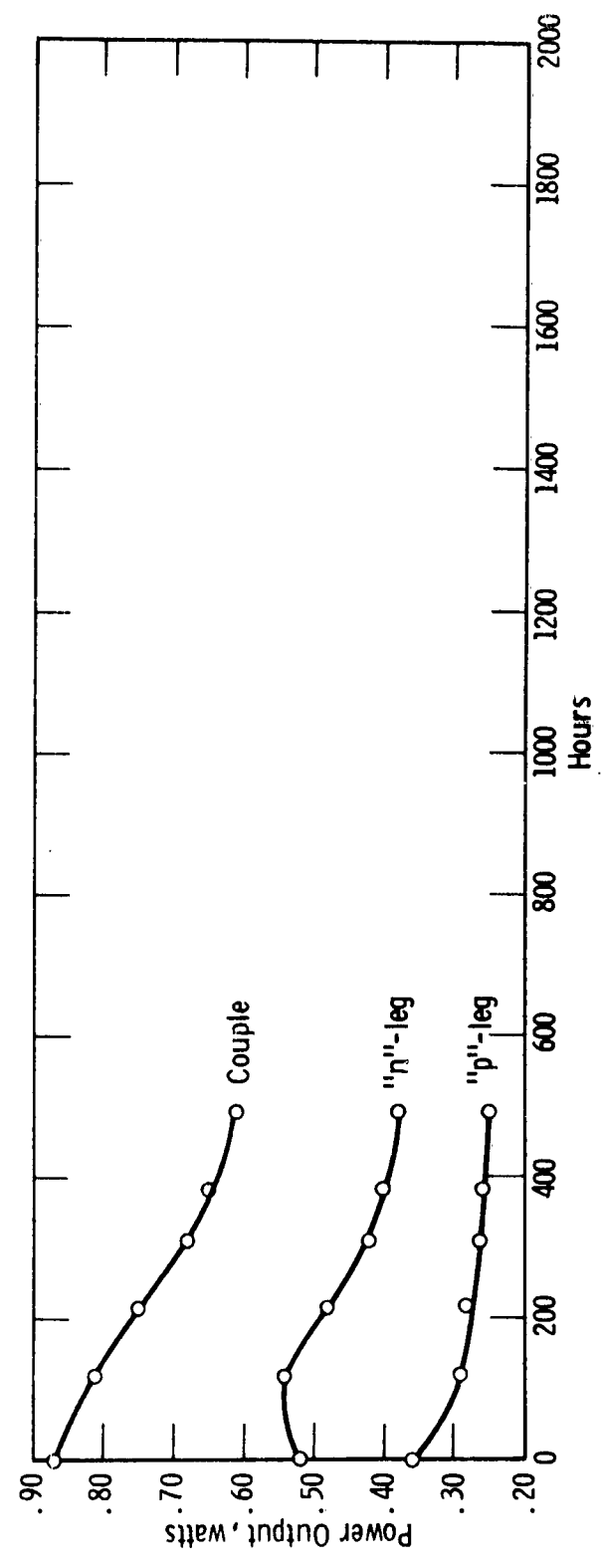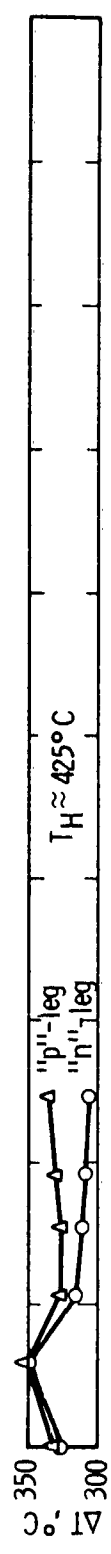
Couple RJ-26, Argon atmosphere

EXHIBIT 10

CURVE 522944

10 Thermal Cycles

$T_H \approx 425°C$

Resistance, Internal, milliohms

ΔT, °C

Power Output, watts

Hours
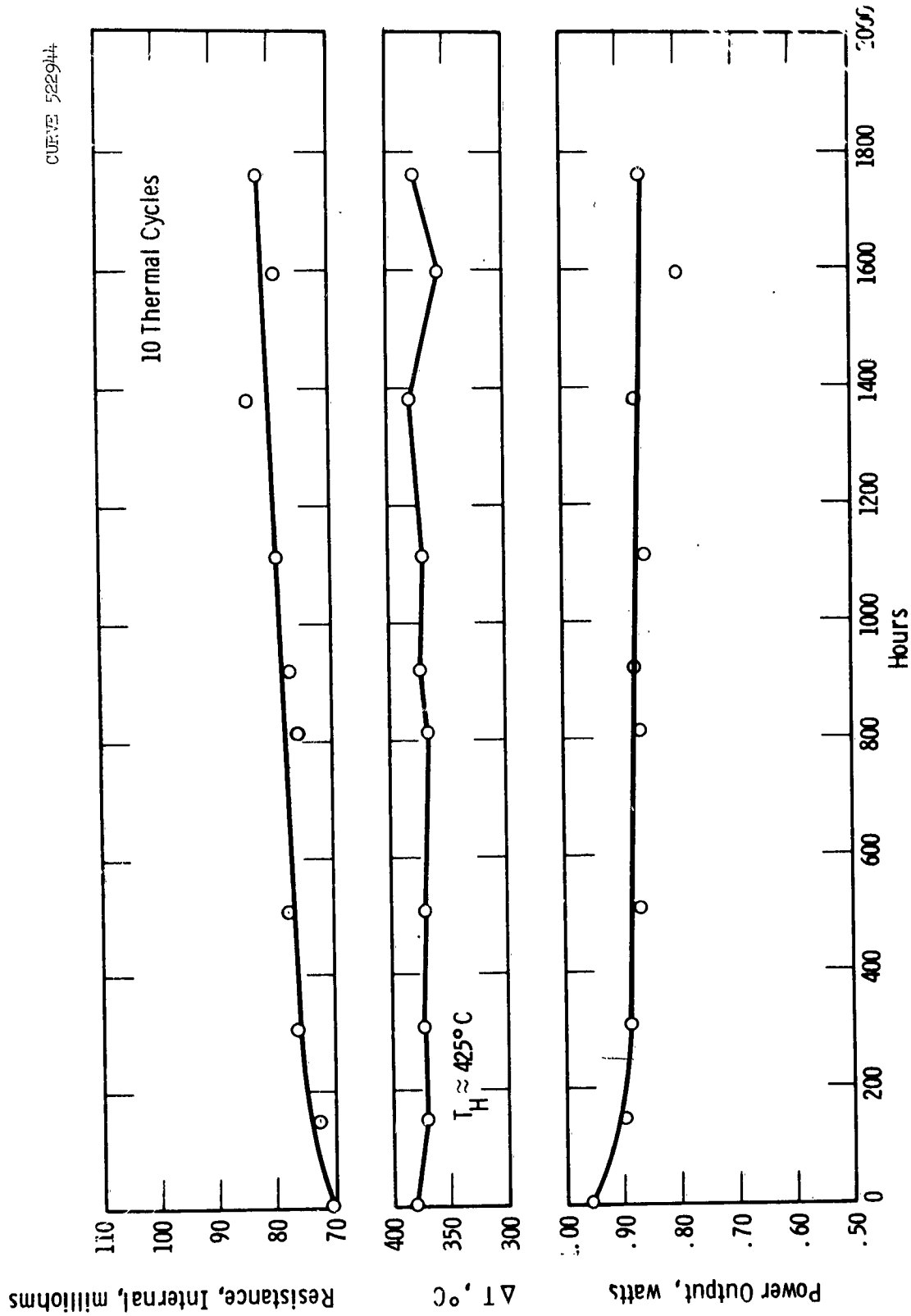
Module X-13, Argon-hydrogen atmosphere   Four couples

EXHIBIT 11

CURVE 522945

8 Thermal Cycles

$T_H \approx 425°C$

Resistance, Internal, milliohms

ΔT, °C

Power Output, watts

Hours
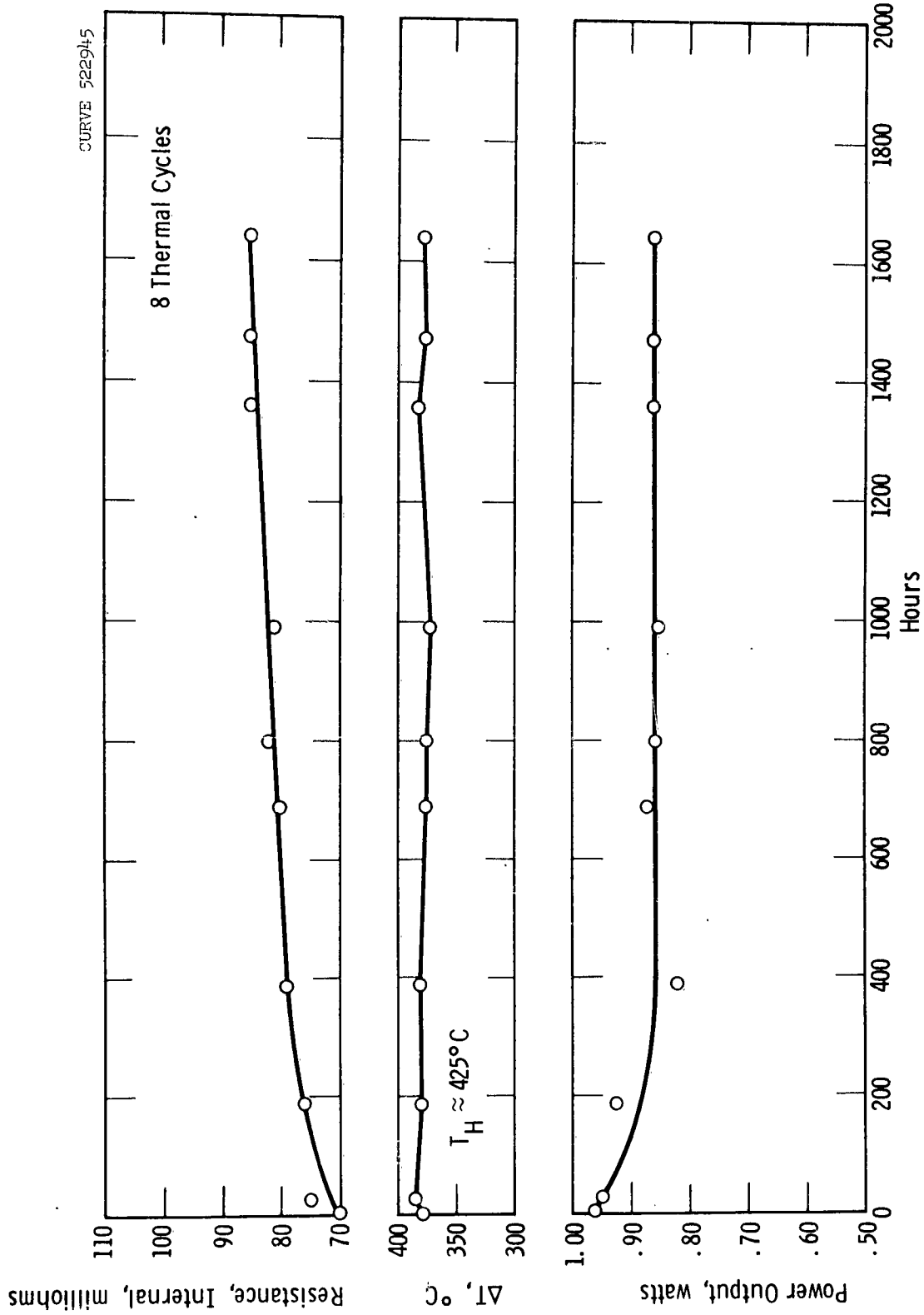
Module X-14, Argon-hydrogen atmosphere   Four couples

EXHIBIT 12

EXHIBIT 13. Description of InSbTe Thermocouples

Couple No.	Type of Couple Material "p"-leg	"n"-leg	Pellets Dimensions	Hot Strap Material	Hot-Side Barrier Layer on Pellets "p"-leg	"n"-leg	Hot Side Contact	Cold Side Contact
RJ-12	InSbTe (3384)	PbTe (3130)	1/4"Sq. x 1/2" High	Copper Plasma Sprayed with Ni	Plasma-Sprayed Fe-Ni	Plasma-Sprayed Co-Ni	Au-In Alloy	Ultrasonic Sn
RJ-20	InSbTe (3384)	PbTe (3130)	1/4"Sq. x 1/2" High	Copper Plasma Sprayed with Ni	Plasma-Sprayed Fe-Ni	Plasma-Sprayed Co-Ni	Au-In Alloy	Ultrasonic Sn (thin braids)
RJ-18	InSbTe (3384)	PbTe (3130)	1/4"Sq. x 1/2" High	Copper Plasma Sprayed with Ni	Plasma-Sprayed Nicrobraz 10	Plasma-Sprayed Co-Ni	Au-In Alloy	Ultrasonic Sn
RJ-13	InSbTe (3384)	None	1/4"Sq. x 1/2" High	Copper plasma Sprayed with Ag-Nicrobraz 10	None	None	Pellet to Ag-Nicro-braz 10 layer	Ultrasonic Sn
RJ-26	InSbTe (3384)	PbTe (3419)	1/2"x 1/4"x 1/4"High	Nickel: 1/2 Plasma Sprayed with Ag-Nicro-braz 10	None	None	InSbTe Pellet to Ag-Nicro-braz 10 layer.PbTe pellet to Ni strap.	Ultrasonic Sn

VAPORIZATION OF ZINC ANTIMONIDE

by

Chikara Hirayama

ABSTRACT

The vapor pressure of ZnSb between 658° and 745°K may be expressed by the $\log p_{atm} = -\boxed{8765 \pm 316} 1/T + 7.71 \pm 0.51$. The heat of reaction for $ZnSb(s) = Sb(s) + Zn(g)$ is $\Delta H_{298} = 40.81 \pm 1.5$ kcal/mole, and the heat of formation of ZnSb is $\Delta H_f^\circ + -9.62 \pm 1.5$ kcal/mole.

VAPORIZATION OF ZINC ANTIMONIDE

I. INTRODUCTION

The thermoelectric properties of ZnSb have been recently reviewed by Miller.[1] This compound is known to be a useful p-type material, whose crystal structure[2] is one of a distorted diamond structure with 16 atoms per unit cell. The compound ZnSb forms peritectically[2,3] and it is known[4] that there is only a limited range of solid solution in the region of this compound.

Zinc antimonide dissociates according to the reaction $ZnSb(s) = Sb(s) + Zn(g)$. The rate of volatilization of ZnSb at constant temperature is time dependent, so that it is necessary to obtain the initial rate of volatilization to calculate the true vapor pressure of the compound, ZnSb, when the pressure is measured by the effusion and free evaporation methods. It is possible to determine the vapor pressure of the above reaction, in which the volatile species is Zn, by the effusion method by measuring the rate of evaporation through a small orifice over a suitable short length of time on a large sample. This is justified in that the rate of evaporation decays exponentially in the initial stage as a function of Exp $(-t/\tau)$, where t is the time and τ is the time constant for a given sample. If $t/\tau \ll 1$ the determined rate of evaporation for a given experiment will be identical to the initial rate within experimental accuracy.

The thermodynamic data on ZnSb is limited, and a doubtful value of -36 kcal/mole is recorded[5] for the heat of formation. We have therefore undertaken to measure the vapor pressure of this compound, and to recalculate the heat of formation.

II. EXPERIMENTAL

The apparatus consisted of a 30 inch long vertical tube. This tube consisted of a 22 inch long, flanged Pyrex brand pipe of 1.5 inch I.D. (Corning Glass Works), to which was sealed a flat-bottomed mullite tube of 1-1/8 inch I.D., and eight inches long. A stainless steel flange, containing the iron-constantan thermocouple and a hook for suspending the sample, was sealed to the flanged top of the Pyrex tube. A gasket of Viton-A (E. I. du Pont) was used to facilitate a vacuum seal. The tube was connected to a vacuum system just below the flanged top. Allowance was made also for introduction of argon to the system to break the vacuum.

The mullite section was heated by raising a tube furnace over it. The temperature of the furnace was controlled to $\pm 2°$ or better, and the bottom four inch section of the tube was at the same temperature.

The Knudsen effusion cells were machined from graphite rods supplied by the National Carbon Company. The dimensions were 1-1/8 inches high, 3/4 inch diameter with wall thickness of approximately 3/16 inch. The cap, on which was drilled the orifice, was approximately 1/4 inch thick. Two different orifice diameters were used, namely 0.125 and 0.0625 inch. The Clausing correction[6] was used to calculate the effective orifice area. The cells were heated above 850°C in a vacuum of approximately 1×10^{-6} mm Hg for several hours until constant weight was obtained.

To obtain the effusion rate, the Knudsen cell was contained in a silica cup which was placed on a platinum pan. The pan was then lowered into the mullite tube. The thermocouple was placed adjacent to the cell. The system was flushed several times with oxygen-free argon, and finally filled with the latter. The sample was then heated by raising the furnace over

the tube and allowed to come to constant temperature. The time required was 20 to 30 minutes. The system was subsequently evacuated to about 3×10^{-5} mm Hg in about three minutes. The pressure during any run was maintained between 5×10^{-6} and 3×10^{-5} mm Hg. Check runs indicated no detectable loss of material during the heat-up time in the argon atmosphere. Each run was terminated by breaking the vacuum with argon, and lowering the furnace to cool the tube with a forced draft. The effusion rate was determined from the weight loss over the heating period under vacuum.

A sample of approximately one gram of ground material was used for each run. The time constant for the 0.125 inch diameter orifice at 695°K was 10^5 seconds. This was the lowest time constant of all the runs. The values of the rate of weight loss calculated from the weight loss in Table I are equal to the initial rate within experimental accuracy.

The ZnSb was kindly supplied by Dr. R. Mazelsky.* The material was prepared by melting stoichiometric quantities of zinc and antimony at about 750°C in an evacuated Vycor tube which was subsequently air quenched. The material was ground, then cold-pressed and sintered at 500°C in an evacuated Vycor tube. The x-ray powder diffraction pattern showed only the ZnSb lines with crystal parameters a = 6.161 Å, b = 7.741 Å, c = 7.986 Å.

The volatile species was determined by heating the zinc antimonide in a vacuum of approximately 10^{-5} mm Hg up to temperatures of 600°C. The x-ray powder diffraction patterns of the condensate showed only the zinc lines when approximately 10% of the solid was volatilized.

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* Westinghouse Research Laboratories

III. RESULTS

The vapor pressure, in atmospheres, was calculated according to the equation $p_{atm} = 0.02255 \ (m/At)(T/M)^{1/2}$ where m is the weight loss in grams, t the effusion time in seconds, A the effective orifice area, T the absolute temperature and M the atomic weight of zinc. The data are recorded in Table I. The pressure in mm Hg is also recorded. Figure 1 shows the plot of log p_{atm} versus $1/T$.

In view of the good fit of the data obtained with the two different orifice areas, it may be concluded that the accomodation coefficient is very close to unity. The dynamic pressure should therefore be identical to the equilibrium vapor pressure.

A least squares treatment of the data gives the equation:

$$\log p_{atm} = (8764 \pm 316) \ 1/T + 7.71 \pm 0.51 \ .$$

The heat of reaction calculated from the slope of the equation is $\Delta H = 40.11 \pm 1.45$ kcal/mole, where the value is assigned to the median temperature of $700°K$.

Using the heat capacity data given by Kelley[7] for $ZnSb(s)$, $Sb(s)$, and $Zn(g)$ the heat of reaction at $298°K$ is found to be $\Delta H_{298} = 40.81 \pm 1.5$. The last number is rounded off to one decimal place since the heat capacity equation for ZnSb is reported to be approximate. The heat of sublimation for zinc[8] at $298°K$ is 31.189 kcal/mole, so that the heat of formation of zinc antimonide from the solid elements, e.g., for the reaction $Zn(s) + Sb(s) = ZnSb(s)$ is $\Delta H_f = -9.62 \pm 1.5$ kcal/mole. This value is considerably lower than the -36 kcal/mole recorded by Rossini, et al.[5]

IV. ACKNOWLEDGEMENT

We thank Dr. R. Mazelsky for supplying the ZnSb and for discussions.

V. REFERENCES

1. R. C. Miller, in "Thermoelectricity: Science and Engineering," ed. R. R. Heikes and R. W. Ure, Jr., Interscience Publishers, New York, 1961, pp. 405-407.

2. M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd Ed., McGraw-Hill, New York, 1958, pp. 1182-1185.

3. R. L. Eisner, R. Mazelsky and W. A. Tiller, J. Appl. Phys., 32, 1883 (1961).

4. I. M. Pilat, L. D. Chizh and S. Yu. Voityshew, Zhur. Tekh. Fiz. 28, 786 (1958).

5. F. D. Rossini, D. D. Wagman, E. H. Evans, S. Levine and I. Jaffe, Natl. Bur. Stds., Circ. 500 (1952).

6. S. Dushman, "Scientific Foundation of Vacuum Technique," John Wiley and Sons, Inc., New York, 1949, pp. 99.

7. K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy," Bur. Mines Bull. 584, 1960.

8. K. K. Kelley, ibid., Bull. 383, 1935.

TABLE I.   VAPOR PRESSURE OF ZnSb

Temp., °K	Time, Sec.	Weight Loss, mg	Eff. orifice area, cm^2 x 10^3	p, mm Hg x 10^3	p, atm. x 10^6
658	7950	6.5	27.84	1.60	2.10
665	6420	8.3	27.84	2.54	3.34
682	3140	10.0	27.84	6.31	8.31
695	1425	5.2	27.84	7.33	9.64
673	4360	1.4	4.44	3.98	5.24
692	6090	4.5	4.44	9.29	12.22
703	9860	11.6	4.44	14.90	19.61
722	3330	8.7	4.44	33.48	44.05
739	3620	14.0	4.44	50.16	66.00
745	1500	7.0	4.44	60.89	80.12
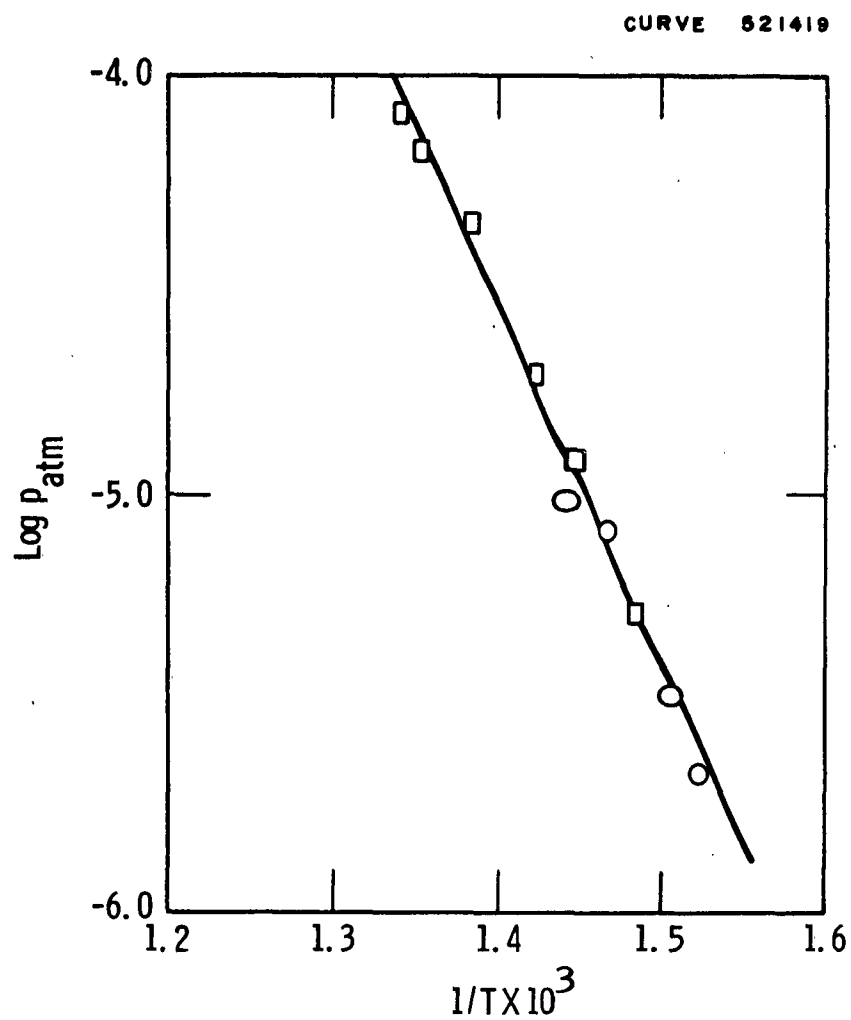
Fig. 1—Vapor pressure of ZnSb as function of temperature

□ 4.44×10^{-3} cm^2 orifice

○ 27.84×10^{-3} cm^2 orifice

THE VAPOR PRESSURE OF GERMANIUM TELLURIDE

by

Chikara Hirayama

ABSTRACT

The vapor pressure of GeTe over the temperature range of 680°
to 837°K is expressed by $\log p_{atm} = -(10{,}255 \pm 451)\, 1/T + 8.255 \pm 0.598$.
The heat of sublimation is 46.86 ± 2.06 kcal/mole.

THE VAPOR PRESSURE OF GERMANIUM TELLURIDE*

I. INTRODUCTION

The germanium-tellurium system and the thermoelectric properties of germanium telluride have been recently reviewed by Miller.[1] Only a single compound, GeTe, with a melting point of 725°C, has been known to be present in this system.[2] However, a recent detailed study[3] of this system has shown the compound to be congruent melting and of composition $GeTe_{1.025}$. Germanium telluride undergoes a phase transformation[4] at about 440°C from the low-temperature rhombohedral form to the cubic.

The thermodynamic properties of $GeTe(g)$ have been computed by Kelley,[5] based on the spectroscopic data[6] for this compound. The thermodynamic properties of $GeTe(s)$ are still lacking.

In view of the interesting thermoelectric properties of the "pure" and bismuth-doped $GeTe$[1] at temperatures above 400°C, we have undertaken to measure the vapor pressure of germanium telluride. The heat of sublimation thus enables one to calculate the thermodynamic properties of $GeTe(s)$. This information adds further to the high temperature thermodynamic properties and volatility characteristics of intermetallic compounds of tellurium.

II. EXPERIMENTAL

The apparatus consisted of a 30 inch long vertical tube. This tube consisted of a 22 inch long, flanged Pyrex brand pipe of 1.5 inch I.D. (Corning Glass Works), to which was sealed a flat-bottomed mullite tube of

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1-1/8 inch I.D., and 8 inches long. A stainless steel flange, containing

the iron constantan thermocouple and a hook for suspending the sample, was

sealed to the flanged top of the Pyrex tube. A gasket of Viton-A (E. I.

duPont) was used to facilitate a vacuum seal. The tube was connected to a

vacuum system just below the flanged top. Allowance was made also for intro-

duction of argon to the system to break the vacuum.

The mullite section was heated by raising a tube furnace over it.

The temperature of the furnace was controlled to $\pm$ 2° or better, and the

bottom four inch section of the tube was at the same temperature.

The Knudsen effusion cells were machined from graphite rods supplied

by the National Carbon Company. The dimensions were 1-1/8 inch high, 3/4 inch

diameter with wall thickness of approximately 3/16 inch. The cap, on which

was drilled the orifice, was approximately 1/4 inch thick. Three different

orifice diameters were used, namely, 0.250, 0.125, and 0.0625 inch. The

Clausing correction[7] was used to calculate the effective orifice area. The

cells were heated above 800°C in a vacuum of approximately 1 x 10^{-6} mm Hg

for several hours until constant weight was obtained.

To obtain the effusion rate, the Knudsen cell was contained in a

silica cup which was placed on a platinum pan. The pan was then lowered

into the mullite tube. The thermocouple was placed adjacent to the cell.

The system was flushed several times with oxygen-free argon, and finally

filled with the latter. The sample was then heated by raising the furnace

over the tube and allowed to come to constant temperature. The time required

was 20 to 30 minutes. The system was subsequently evacuated to about

3 x 10^{-5} mm Hg in about three minutes. The pressure during any run was main-

tained between 5 x 10^{-6} and 3 x 10^{-5} mm Hg. Check runs indicated no

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detectable loss of material during the heat-up time in the argon atmosphere. Each run was terminated by breaking the vacuum with argon, and lowering the furnace to cool the tube with a forced draft. The effusion rate was determined from the weight loss over the heating period under vacuum.

The germanium telluride was prepared* similar to that described by Johnston and Sestrich[8] from stoichiometric amounts of germanium and tellurium, and the material was crushed and ground to a powder. A wet analysis indicated 36.2% Ge and 63.75% Te (theoretical: Ge = 36.21%, Te = 63.79%). An x-ray powder diffraction pattern indicated no unreacted metals present, and the lattice parameter agreed with that reported;[8] i.e., $a = 5.98$ Å.

Separate samples of germanium telluride were volatilized at 525° to 650°C. The x-ray diffraction patterns of the condensate indicated the presence of GeTe only. Because we do not have mass spectroscopic data, the volatile species is assumed to be the monomer GeTe.

III. RESULTS

The results of the determinations are summarized in Table I, with the data recorded in the order of runs. The vapor pressure was calculated with the aid of the equation:

$$p = 0.02255 \ (m/At)(T/M)^{1/2} \tag{1}$$

where p is in atmospheres, m the weight loss in grams, t the effusion time in seconds, A the effective orifice area, T the absolute temperature and M the molecular weight of GeTe. The pressure in mm Hg is also recorded.

A least squares treatment of the data in Table I gave the equation:

$$\log p_{atm.} = -(10,255 \pm 451) \ 1/T \pm 8.255 \pm 0.598 \tag{2}$$

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* The GeTe was kindly supplied by Mr. Y. Ichikawa, Westinghouse Electric Corporation, Youngwood, Pennsylvania.

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with a linear regression coefficient of 0.992. The linear relationship is therefore excellent, and the heat of sublimation over the temperature range studied is constant. The heat of sublimation calculated from the slope of the line is $\Delta H_{sub.} = 46.86 \pm 2.06$ kcal/mole.

The good linear relationship of the data obtained with cells of three different effective orifice areas show that the accommodation coefficient is very close to unity. In view of the small ratio of orifice area to surface area of the vaporizing solid, it can be concluded that the equilibrium vapor pressure of germanium telluride is identical to the measured dynamic pressure, p.

IV. BIBLIOGRAPHY

1. R. C. Miller, in "Thermoelectricity: Science and Engineering," Ed. R. R. Heikes and R. W. Ure, Jr., Interscience Publishers, New York, 1961, pp. 434-439.

2. M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd Ed., McGraw-Hill, New York, 1958.

3. J. P. McHugh and W. A. Tiller, Trans. Met. Soc. A.I.M.E., 218, 187 (1960).

4. K. Schubert and H. Fricke, Z. Metal., 44, 459 (1953).

5. K. K. Kelley, "Contributions to the data on theoretical metallurgy," U. S. Bur. Mines Bull. No. 584 (1960).

6. G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd Ed., Van Nostrand, New York, 1950.

7. S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, Inc., New York, 1949, p. 99.

8. W. D. Johnston and D. E. Sestrich, J. Inorg. Nucl. Chem., 19, 229 (1961).

TABLE I - VAPOR PRESSURE OF GeTe

T, °K	Time, Sec.	Wt. Loss, mg.	Eff. Orifice Area cm^2 x 10^2	P, mm Hg (calc.)	P, atm. (calc.)
725	10300	10.2	2.784	1.16×10^{-3}	1.52×10^{-6}
702	13520	5.4	2.784	4.60×10^{-4}	6.05×10^{-7}
751	8360	22.2	2.784	3.17×10^{-3}	4.17×10^{-6}
767	5150	18.2	2.784	4.26×10^{-3}	5.61×10^{-6}
787	3480	23.8	2.784	8.34×10^{-3}	1.10×10^{-5}
680	18900	2.0	2.784	1.19×10^{-4}	1.57×10^{-7}
816	2100	38.4	2.784	2.27×10^{-2}	2.99×10^{-5}
796	6060	16.4	0.444	2.08×10^{-2}	2.74×10^{-5}
837	3310	44.6	0.444	1.06×10^{-1}	1.39×10^{-4}
823	3340	28.5	0.444	6.69×10^{-2}	8.80×10^{-5}
683	10620	4.7	14.11	9.94×10^{-5}	1.31×10^{-7}